BUA Report on Liquefied petroleum gas

Summary and conclusions

Ecological aspects

Occurrence and distribution among the compartments

Liquefied Petroleum Gas (LPG) is a natural constituent of crude oil and natural gas. LPGs obtained in crude oil or natural gas production are reblended into the stabilized crude oil and sent to the mineral-oil refineries. Propane and butane are separated in special distillation towers, the gas recovery units. They are marketed as LPG by the petroleum industry either directly as propane and butane or as mixtures of the two.

According to the published mineral-oil data the LPG production of the refineries amounted to

1991 2 358 000 t
1992 2 583 000 t

The average LPG production for the years 1987-1992 can be calculated to 2.7 % (m/m) on crude.

LPG consists mainly of propane, isobutane and butane. It may also contain other hydrocarbons, in concentrations above 1 % (mm) ethane, propene, butenes and isopentane. In Germany the butadiene content of LPG usually is below 0.1 % (m/m). The German LPG standards require a minimum level of 95 % (m/m) of C_3- or C_4-hydrocarbons respectively. The composition of commercially used LPGs may vary within these limits to a considerable amount.

This BUA report mainly refers to the main LPG constituents propane, isobutane und butane. Ethane, propene, butenes and isopentane will not be covered in detail.

1991 appr. 4.1 million t of LPG were used in Germany:

- In the refineries appr. 30 % were blended into gasolines. This portion is statistically classified as gasoline, for example in "Amtliche Mineralöldaten für die Bundesrepublik Deutschland (Official Mineraloil-Data of the Federal Republic of Germany) and "MWV Mineralöl-Zahlen (MWV Mineraloil-Data)".
- Its main use was as a fuel for heating and illumination purposes (appr. 47 %), a minor amount (appr. 1.5 %) was used for motor operations. Due to their small amounts the use as automotive gas (appr. 3 000 t) and as aerosol propellent (appr. 22 250 t) are statistically not listed separately, but are included in the aforementioned figures.
- Due to existing economic incentives an essential portion (appr. 21 %) was used as feed stock for steamcracking Operations.

The natural emissions of LPG into the atmosphere and hydrosphere cannot be quantified. The physico-chemical properties (vapor pressure, Henry's constant, chemical structure) indicate that all LPG emitted into the various compartments will almost completely enter the atmosphere after short periods of time.

Based on the available data the total release into the atmosphere can roughly be estimated to appr. 215 240 t/a for the year 1991. This figure does not include any emissions from combustion processes. The combustion of gasolines in car engines will additionally provide emissions of appr. 42 000 t/a of saturated and unsaturated C_3- and C_4-hydrocarbons in the Federal Republic of Germany.

In ocean water average concentrations of C_2-C_4-hydrocarbons were determined in the ng/l range. Data are not available for the rivers of the Federal Republic of Germany.

In the Federal Republic of Germany maximal concentrations of 22.6 µg/m^3 of propane, 26.6 µg/m^3 of isobutane and 55.7 µg/m^3 of butane were found in air samples.

During 1984/1985 a very extensive study investigated workplaces involved in the manufacture and distribution of gasoline. On the basis of 540 personal gasoline exposure measurements in 13 European countries the C_3-C_4-concentrations in gasoline vapor amounted to appr. 37 % (m/m). 8 hour time-weighted average exposures of 1.6 mg/m^3 of propane, 12.1 mg/m^3 of isobutane and 26.6 mg/m^3 of butane were determined as average figures in long-term personal samples at 12 workplaces (318 measurements). At self-service stations customers were exposed to maximal concentrations of 8.2 mg/m^3 of propane, 34.4 mg/m^3 of isobutane and 74.0 mg/m^3 of butane (2 min time-weighted average) as average of 21 measurements.

Degradablity

Bacteria capable of growth on hydrocarbons which are available in LPG suggest the possible degradation of these hydrocarbons.

The hydrolytic degradation of the simple alkanes/alkenes is not possible due to their chemical structure.

Calculation of the reactivities towards OH radicals result in atmospheric half-lives between 0.3 and 13.3 days.

XIV

Bioaccumulation, geoaccumulation

According to the available values for the log P_{OW} from 1.74 to 2.89 - only isopentane with an average content of 1.2 % (m/m) in butane has a log P_{OW} of 3.21 - appreciable bioaccumulation seems unlikely. In addition the physico-chemical data do not indicate any geoaccumulation.

Ecotoxic effects

There are no studies available regarding the effects of LPG on aquatic organisms.

Mycobacterium vaccae and *Mycobacterium phlei* were capable of growth on propane, isobutane and butane. The lysis of whole cells and cell-wall fragments of *Micrococcus lysodeikticus* by egg-white lysozyme was inhibited by the same hydrocarbons. The inhibitory action of hydrocarbons present in LPG on the enzymatic catabolism of bacterial spores was demonstrated.

According to the available study results alkanes have only minor effects on plants. The series of alkenes contains differently effective hydrocarbons from the phytotoxic ethene over the still active propene and 1-butene to the inert 2-butenes.

Toxicological aspects

There are no special reports of toxicity studies on LPGs. However, information published on the major components propane, isobutane and butane is useful for predicting the possible toxicity of LPG.

The hydrocarbons are primarily resorbed by the respiratory tract and partly exhaled unchanged via the lungs.

Secondary and tertiary alcohols are obtained by the microsomal hydroxylation of the lower members of the alkanes. The secondary alcohols are oxidized to ketones by the dehydrogenase system, while the tertiary alcohols are rather stable and will only be metabolized to a small extent.

In mammals propane, isobutane and butane are considered as slightly toxic after acute inhalative application. The LC_{50} for the rat has been reported as 658 mg/l/4 h for butane, 1379 mg/l/15 min for isobutane and > 1465 mg/l/15 min for propane. Acute intoxication is manifested in CNS depression. Butane demonstrated greater narcotic and lethal effects than isobutane. After inhalation cardiac sensitization to adrenalin in dogs has been reported.

Studies on genotoxicity of propane and butane did not show any mutagenic activity in bacterial systems with Salmonella typhimurium (TA 98, TA 100, TA 1535, TA 1537, TA 1538) with and without metabolic activation.

LPG vapor is not a respiratory irritant for man. Increasing concentration and exposure time will result in narcotic effects. High concentrations may result in loss of consciousness, convulsions and even asphyxiation as a consequence of oxygen deficiency. The narcotic effect of butanes is greater than with propane.

Operating experiences have shown that propane, isobutane and butane are non-irritating and without a sensitizing effect. In direct contact to the skin erythema and oedema formation as well as necrosis by cold burns were observed.

XVI

Longtime exposed workers at a LPG filling station reported symptoms such as throat dryness, dry cough, excitability and sometimes giddiness. Medical investigation revealed harsh respiration, dyspnoea, tachycardia, sometimes joined with extrasystolic arrhythmia and pain to epigastrium palpation.

There are no data available on repeated application, clastogenicity, cancerogenicity and reproduction toxicity.

Recommendations

Ecotoxicity

The available studies on the ecotoxic effects and the behaviour in the environment are considered adequate for the evaluation of the three main LPG-constituents propane, isobutane and butane.

Toxicity

The three main constituents propane, isobutane and butane are inert gases which lead to intoxications only at very high concentrations, particularly in case of oxygen deficiency in the breathing air. Specific toxic effects will not be expected so that the missing investigations on repeated application, clastogenicity, cancerogenicity and reproduction toxicity are not required.

In so far as the LPG contains other hydrocarbons in relevant quantities these must be considered in the toxicological evaluation.

Carrying out further toxicological studies with LPG samples is not regarded as useful because the composition varies and further relevant evidence cannot be expected.

SERIES EDITOR: R. SNYDER

Ethel Browning's Toxicity and Metabolism of Industrial Solvents

SECOND EDITION

VOLUME I: HYDROCARBONS

EDITOR: R. SNYDER

Joint Graduate Program in Toxicology, Rutgers College of Pharmacy, Rutgers, The State University of New Jersey, and The University of Medicine and Dentistry of New Jersey, Robert Wood Johnson Medical School, Piscataway, NJ 08854, U.S.A.

1987

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3.4. *n*-Butane

LAWRENCE K. LOW, J. RALPH MEEKS and CARL R. MACKERER

Synonym: normal butane

CAS-number: 106-97-8

Structural formula: $CH_3—CH_2—CH_2—CH_3$

Molecular formula: C_4H_{10}

Molecular weight: 58.123

Properties
boiling point: −0.50° C
melting point: −138° C
vapor pressure (18.8° C): 2 mmHg (0.267 kPa)
vapor density (air = 1): 2.07
specific gravity (liquid density) (−25° C): 0.573
flash point: −60.0° C (−76° F)
conversion factors: 1 p.p.m. = 2.37 mg/m^3 = 0.00237 mg/l
1 mg/m^3 = 0.422 p.p.m.
solubility: relatively insoluble in water, 61 μg/ml at 20° C; very soluble in alcohol and ether, log $P_{octanol} = 2.89$
maximum allowable concentration: 800 p.p.m. (TWA, ACGIH 1984–1985)

Ethel Browning's Toxicity and Metabolism of Industrial Solvents, 2nd edition.
Vol. 1: Hydrocarbons. R. Snyder, editor

ECONOMY, SOURCES AND USES

PRODUCTION

n-Butane and isobutane are produced from raw natural gas and from petroleum streams obtained by catalytic cracking, catalytic reforming, and other refining processes. Liquid butane is often recovered from the feedstock gas through a 'debutanizing' process involving refrigeration, adsorption, expansion, compression, fractionation, and other cryogenic steps (Boesiger et al 1980).

INDUSTRIAL USES (Boesiger et al 1980)

1. As feedstock in the production of ethylene (thermal cracking process) and in the production of 1,3-butadiene (precursor for synthetic rubber).
2. In the blending of gasoline or motor fuel.
3. In the synthesis of high octane blend stocks of motor fuel (the butanes, particularly isobutane, are alkylated with C3–C4 olefins to produce highly branched C7–C8 fuel blends).
4. In the synthesis of acetic acid, maleic anhydride, isobutane, and other chemicals.
5. As a constituent in liquified natural gas (LPG) and substitute natural gas (SNG).
6. As a refrigerant and aerosol propellant.
7. As a solvent in the liquid–liquid extraction of heavy oils in deasphalting processes.

BIOCHEMISTRY

ESTIMATION

In the atmosphere

Measurement of *n*-butane in the atmosphere has been carried out by gas chromatography (GC) and headspace techniques (Westberg et al 1974). In addition, colorimetric detector tubes, permeation tubes, and direct-reading gas analyzers have been employed to quantitate the levels of *n*-butane in the air (American Conference of Governmental Industrial Hygienists 1978).

In blood and tissues

Detection and quantitation of butane in the tissues of rats and mice have been carried

out by GC methods. Tissue (brain, liver, kidney, spleen, and perinephric fat) is homogenized and extracted with isooctane prior to GC analysis (Shugaev 1969).

METABOLISM

Absorption and distribution

Inhalation studies by Shugaev (1969), in which rats and mice were exposed to lethal concentrations (27.8–29%), revealed that *n*-butane is absorbed and distributed to various tissues. After 4 h of respiratory exposure, surviving rats were sacrificed and tissues analyzed; concentrations of butane were found to be highest in perinephric fat (2086 p.p.m.), then brain (750 p.p.m.), spleen (522 p.p.m.), liver (492 p.p.m.), and kidney (441 p.p.m.). In mice exposed to 2 h of butane vapors, the brain levels of *n*-butane were found to be 779 p.p.m. In both rats and mice the brain concentrations of *n*-butane correlated with the degree of CNS depression and narcosis. Dermal absorption of *n*-butane vapors has not been reported. However, dermal penetration of butane would not be expected to occur to any large extent since skin contact is transient because of volatility.

Pharmacokinetics

Pharmacokinetic studies of *n*-butane have not been reported. Based on the kinetic studies of Filser et al (1983) with ethane and *n*-pentane, the elimination half-life of *n*-butane can be expected to be closer to that of *n*-pentane ($t_{\frac{1}{2}}=0.13$ h, at nonsaturating concentrations). It is not known whether *n*-butane follows dose-dependent pharmacokinetics like its next higher homolog, *n*-pentane. Hydroxylation of butane has been demonstrated to occur in rat liver microsomes to yield 2-butanol as the major metabolite (Frommer et al 1970). *n*-Butane is the lowest molecular weight alkane that has been demonstrated to substrate-bind with cytochrome P-450. At present, the metabolic fate of *n*-butane in vivo has not been studied extensively. If 2-butanol is the major metabolite formed in mammals, it would be expected to be eliminated in expired air (Pohl 1908). Like other alcoholic metabolites formed from hydroxylation of normal alkanes, 2-butanol may also be conjugated with glucuronic acid or be oxidized to methyl ethyl ketone which in turn is expired (Browning 1965). Because of its volatile nature and based on studies with methane, ethane, and propane, elimination of unchanged *n*-butane by exhalation can be anticipated.

TOXICOLOGY

ANIMAL TOXICITY

Acute

Lethal dose

Since *n*-butane is a gas at room temperature, respiratory toxicity is of primary concern. Lethality has been observed in rats and mice exposed to butane vapors. Shugaev (1969) found the 4-h LC_{50} to be 658 mg/l (278,000 p.p.m.) in rats and the 2-h LC_{50} to be 680 mg/l (287,000 p.p.m.) in mice. Extensive studies by Stoughton and Lamson (1936) yielded similar results: respiratory exposure of mice to 27% (270,000 p.p.m.) for 2 h caused death in 40% of the animals and 310,000 p.p.m. for 2 h caused 60% mortality. In dogs, lethality was observed at concentrations of 200,000–250,000 p.p.m.; anesthesia and relaxation preceded death. Stoughton and Lamson (1936) concluded that there was only a small margin of safety between anesthetic and lethal concentrations. Comparative studies indicate that *n*-butane is somewhat more toxic than isobutane, since the 2-h LC_{50} value for isobutane in mice was 520,000 p.p.m. (Aviado et al 1977).

Narcotic dose

Exposure of mice to 13% *n*-butane caused light anesthesia within 25 min. At a concentration of 22% *n*-butane, light anesthesia was observed within 1 min and complete anesthesia was evident after 15 min. Shugaev (1969) has shown that mixing butane and isobutylene produced an additive narcotic effect in 2 out of 12 mice and a potentiating effect in the remaining 10 animals. In rats, the butane–isobutylene mixture showed a summation of effects in 9 out of 12 animals and a potentiation of effects in the remaining animals.

Chronic

Chronic studies of *n*-butane in animals have not been reported.

Symptoms of intoxication

The heart Several studies have indicated that *n*-butane sensitizes the myocardium to epinephrine-induced cardiac arrhythmias. For example, Chenoweth (1946) showed that exposure of dogs to 1–20% *n*-butane for periods of 2 min to 2 h hypersensitized the heart to ventricular fibrillation induced by epinephrine. Krantz et al

(1948) found that exposure of dogs to concentrations of 15–90% for 10 min caused the heart to be sensitized to epinephrine-induced arrhythmias. Aviado et al (1977) noted hemodynamic changes in dogs inhaling 5000 p.p.m. butane which included decreased cardiac output, left ventricular and aortic blood pressure, stroke volume, and myocardial contractility.

The lungs and skin *n*-Butane has not been reported to cause respiratory or eye irritation in rabbits (Moore 1982). Nuckolls (1933), however, has reported that 21,000–56,000 p.p.m. levels of *n*-butane increased the respiratory rate and sniffing and chewing behavior in guinea pigs. Butane appears to be mildly to moderately irritating to the rabbit skin (Moore 1982).

HUMAN TOXICITY

Limited data is available on the toxicity of *n*-butane to humans. Patty and Yant (1929) found that inhalation of 10,000 p.p.m. for 10 min caused drowsiness in human volunteers. Exposure to higher butane concentrations was not studied. Except for the possibility that liquified butane may cause frostbite when applied directly to the skin, adverse effects related to *n*-butane exposure have not been reported. *n*-Butane has been labeled as a GRAS ('generally recognized as safe') food additive and is found primarily as a volatile component in hair conditioners, blushers, foundation and makeup bases, and shaving creams (Moore 1982).

MUTAGENICITY

Studies carried out using the Ames *Salmonella typhimurium* bioassay in the presence and absence of a metabolic activating system did not show any mutagenic activity for *n*-butane (Stanford Research Institute 1977).

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Light Hydrocarbon Gases: A Narcotic, Asphyxiant, or Flammable Hazard?

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A model used to predict the potency of anesthetic gases is proposed as being applicable to predicting the onset of narcosis from exposure to light hydrocarbon gases (C1 to C3) in a workplace setting. The validity of the model is confirmed using human experience from diving (nitrogen narcosis) and workplace exposure to toluene.

The solubility of a gas or vapor in olive oil must be known to use this predictive model. The air/olive oil partition coefficients of 15 hydrocarbons (C1 to C4, plus hexane and benzene) have been measured and are reported, many for the first time (methane 0.89; ethane 2.1; propane 5.9; and butane 17.1).

The model predicts that the light hydrocarbon gases are not just simple asphyxiants but fast-acting agents inducing narcosis as expressed in loss of judgment, disorientation, dizziness, and light headedness.

The recommendation is made that in addition to an 8-hour time-weighted average exposure limit (1000 ppm, set on a basis of good industrial hygiene practice), a maximum exposure limit is needed. This is set at 10 percent of the lower explosive limit (LEL) on the basis of avoidance of narcosis and recognition of the explosive hazards of the gases. The implications of such a limit in the workplace are discussed. In particular, oil and gas workers who are responding to a combustible gas alarm (set at 10% of the LEL) need to use supplied-air respiratory protection before entering the building where the alarm has tripped. Drummond, I: Light Hydrocarbon Gases: A Narcotic, Asphyxiant, or Flammable Hazard? Appl. Occup. Environ. Hyg. 8(2):120–125; 1993.

Introduction

The threshold limit values (TLV) of the alkanes from nonane (C9) to butane (C4) (with the exception of n-hexane) are set on the basis of narcotic effect and irritation.[1] The values of the 8-hour time-weighted average (TWA) exposure limit increase steadily from 200 ppm for nonane, to 800 ppm for butane, reflecting the reduction in potency for both health effects, as described in the TLV documentation.

Propane, indeed all the C1, C2, and C3 hydrocarbons, saturated and unsaturated, are listed as simple asphyxiants. The preface to the TLV booklet states that these materials "act primarily as simple asphyxiants without other significant physiological effects," and goes on to recommend maintaining a minimum oxygen content of 18 percent by volume, equivalent to 18 kPa partial pressure of oxygen. While the TLV booklet contains a warning about the flammable properties of these gases, the two recommendations for simple asphyxiants and oxygen content of air when combined suggest that an atmosphere of 14 percent by volume of these light hydrocarbon gases can be breathed without significant physiological effect.

Thus there is a dramatic difference in the recommended TLVs for butane and propane, 800 ppm versus 140,000 ppm, a difference which hardly seems justified by any incremental difference in physical or chemical properties.

Some confusion is introduced by the TLV listed for liquified petroleum gas (LPG), which is primarily propane with some butane present. The 8-hour TWA is 1000 ppm, on the basis of "good industrial hygiene practice and to minimize the probability of fire and explosion." It is further stated that concentrations of 100,000 ppm may be tolerated, but induce dizziness in a few minutes.

In addition to an 8-hour TWA TLV, specific information on short-term exposure limits is needed. The nature of these materials, gases, and liquids handled in large volumes at pressures above atmospheric mean that leaks or spills can quickly generate very high concentrations in air. This is recognized in the oil and gas industry by the extensive use of combustible gas alarms to protect expensive installations by warning of approaching danger of fire or explosion. An operator responding to such an alarm knows that the atmosphere of the work area contains at least several thousand parts per million of a hydrocarbon gas. Clear guidance on the air concentrations at which respiratory protection is needed is vital for the confidence and safety of the personnel entering such a situation.

Occupational exposure limits (OEL) are set using a variety of criteria, but human experience, animal testing, and analogy with similar materials are three primary sources of information. The method of analogy is particularly useful where there is a well-understood mechanism of action and

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a pharmacokinetic model which allows evaluation of the differences between similar materials.

Fortunately there is such a model, calibrated by extensive human experience, which is proposed here as being applicable to evaluating the narcotic effects of these hydrocarbon gases in the workplace setting. The model is one used to predict the potency of anesthetic gases.

Anesthetic Gas Model

The history and principles of anesthesiology are described by Kennedy and Longnecker.[2] The general anesthetic gases, which include nitrous oxide, cyclopropane, diethyl ether, chloroform, and halothane, are believed to exert their action by dissolving in the lipid bilayer which forms cell membranes. Certainly their potency can be predicted accurately by their solubility in lipid, as shown by the remarkable graph in Figure 1. The figure shows that many materials not normally considered anesthetics, such as nitrogen and the inert gases, obey the same relationship of dose versus solubility; this shows that a wide range of different materials have a common mode of action. Moreover, the hydrocarbons ethylene and cyclopropane are specifically identified, and it is possible to find in the literature references to the experimental use of methane as an anesthetic.[3] Thus there are both experimental and theoretical reasons to believe that the relationship shown in Figure 1 can be used to predict the concentrations of the light hydrocarbon gases which would cause anesthesia.

The effects of interest in the workplace clearly fall short of surgical anesthesia. However, there are in the literature suggestions that the onset of narcosis is part of a continuum of central nervous system (CNS) effects which includes surgical anesthesia. For example, Sato and Nakajima[4] comment as follows on the relationship of TLVs with the blood/air partition coefficient: ". . . both toluene and xylene . . . are potent CNS depressants, and their toxicities are considered on the basis of a common mechanism, ie, anesthetic action."

In particular the literature on diving thoroughly documents the onset of nitrogen narcosis, which is specifically identified with an anesthetic effect.[5,6] The diving experience allows an estimation of the dose, as a percentage of the anesthetic dose, at which narcotic effects first become apparent. The depth at which nitrogen narcosis is clearly noticeable is about 100 ft (30 m) of water when diving on air.[6-8] This corresponds to a partial pressure of 240 kPa of nitrogen, or about 10 percent of the anesthetic dose.

The anesthetic gas model also allows a qualitative prediction of the speed of action of these materials. Kennedy and Longnecker[2] specifically state that the less soluble in blood, the FASTER the action of the gas. These authors

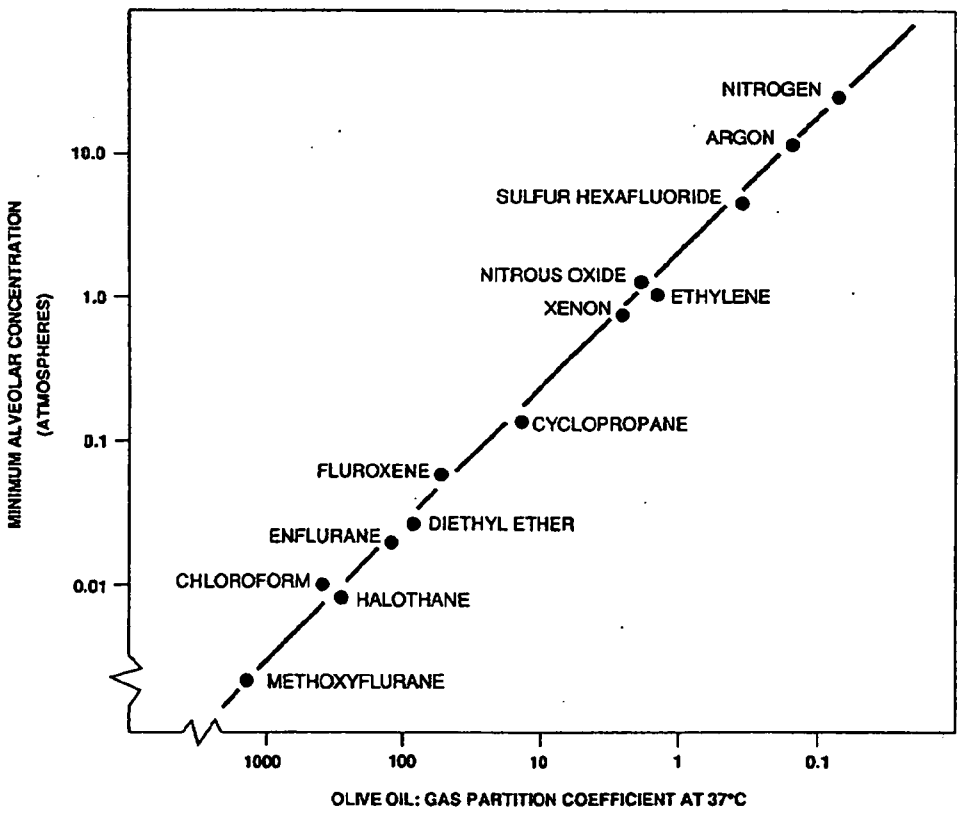

FIGURE 1. The correlation of anesthetic potency with olive oil : gas partition coefficient. The correlation is shown for a number of general anesthetic agents and other gases not normally used for anesthesia. Note the logrithmic scales and excellent correlation over a wide range of oil solubilities and potencies. (Reproduced from Kennedy and Longnecker, in *Goodman and Gilman's The Pharmacological Basis of Therapeutics*, 8th ed, chap 13, Pergamon Press, 1990. Reprinted by permission of McGraw-Hill)

document the rise in concentration of anesthetic gases in the blood of patients; gases which are relatively insoluble in blood, such as nitrous oxide, rise quickly toward equilibrium with the inhaled mixture. Gases which are soluble in blood rise to equilibrium only slowly. For example, nitrous oxide has a blood/air partition coefficient of 0.44[9] and within 5 minutes of exposure arterial blood gas tension rises to 80 percent of the equilibrium value. Yet for diethyl ether with a blood/air partition coefficient of 12, after 5 minutes the corresponding value is less than 10 percent.[2] Confirmation of this information can be found in the diving experience, where the onset on nitrogen narcosis with depth is virtually immediate, nitrogen having a blood/air partition coefficient of 0.015.[9]

Use of the Model for Workplace Exposures

The effect of interest in the workplace is the onset of narcosis, marked by impairment of intellectual and neuromuscular performances. As described above, this is clearly defined from human experience with nitrogen at 10 percent of the anesthetic dose. The power of Figure 1 to predict anesthetic dose from knowledge of oil/air partition coefficients can thus be extended to prediction of the onset of narcosis at 10 percent of the anesthetic dose.

Figure 2 is derived from Figure 1 by changing the scale to cover lower concentrations, and by adding the line marked "narcosis onset" which is drawn parallel to and a factor of 10 lower than the anesthetic dose line. If the oil/air partition coefficient for a particular material is known, then Figure 2 allows prediction of the concentration in air when symptoms of narcosis might be expected to become apparent.

Toluene provides a test of the accuracy and range of this relationship. Toluene is currently undergoing review for a TLV change from 100 to 50 ppm based on reports of altered CNS performance.[10] Given the oil solubility of toluene of 1400,[9] Figure 2 predicts that overt CNS effects would be caused by a concentration in air of 220 ppm. The agreement between this prediction and the value of 100 ppm (where CNS effects are reported to occur) lends strong support to the predictive power of Figure 2 over a wide range of potency.

Also drawn on Figure 2 is a horizontal line corresponding to a concentration of 14 percent, the concentration of an asphyxiant material that would reduce the oxygen content of contaminated air to 18 percent. The two lines intersect at an oil solubility of 1.6. Thus gases and vapors having an oil solubility of greater than 1.6 would be expected to induce narcosis while there is still sufficient oxygen (>18%) in the workplace air; and gases with oil solubilities less than 1.6 would displace oxygen before CNS effects become apparent.

Values for the Oil/Air Partition Coefficients

A survey of the literature revealed a number of compilations of solubility data, none of which covered all the C1 to

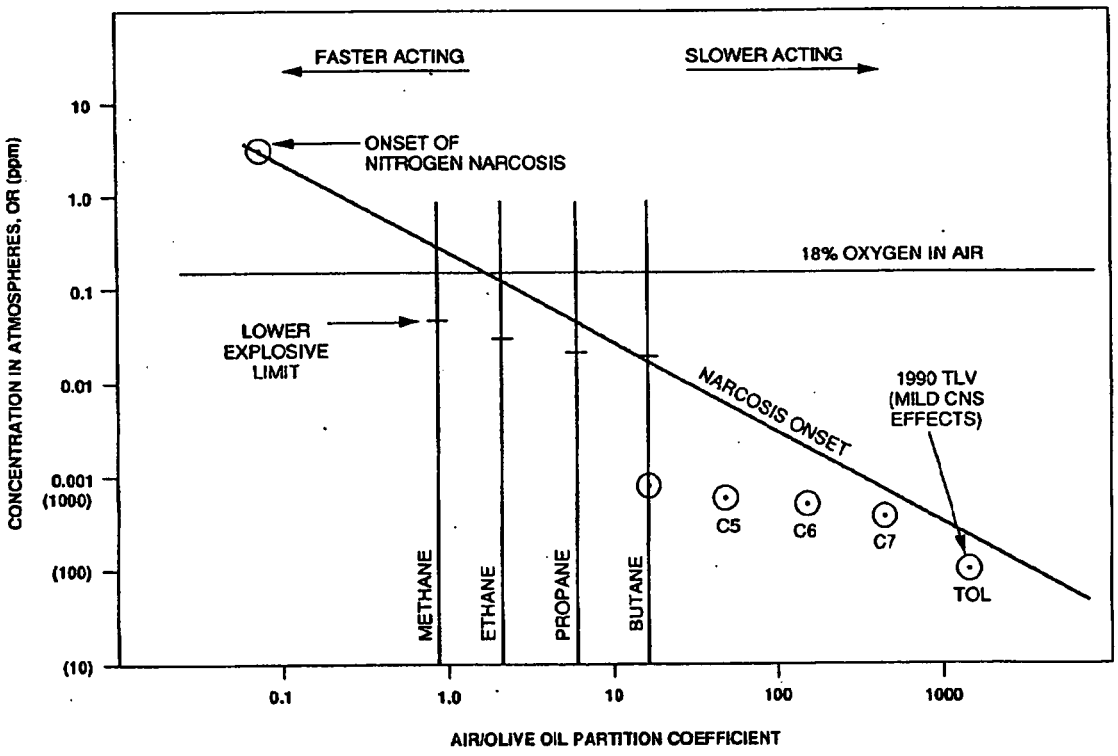

FIGURE 2. The prediction of the concentration in air to induce narcosis from olive oil solubility. The graph allows ready comparison between the ability of a material to form an atmosphere which might be narcosis inducing, explosive, or oxygen deficient. For example, propane has an oil solubility of 5.9, a lower explosive limit of 21,000 ppm, it is predicted to cause overt narcotic effects at 47,000 ppm, and at 140,000 ppm has displaced oxygen to 18 percent.

C4 hydrocarbon gases. Reviews which documented a considerable amount of information were found.[6,9,11-13] Data for all C1 to C4 hydrocarbons which were identified are summarized in Table I.

Because data for the alkanes (ethane, propane, and butane) were not identified, the partition coefficient for 15 hydrocarbon gases was measured by the method of Sato and Nakajima, as described by Perbellini *et al.*[10] A gas mixture containing all 15 gases was used; a gas chromatograph equipped with a 30 m GS-Q Megabore column (J & W Scientific, Folsom, CA) allowed separation of all 15 compounds during each run. Vials of 16.6 ml capacity were used, five empty (standard) vials and five vials containing 2 ml of olive oil. Of the gas mixture, 0.100 ml was injected into each of the ten vials which were kept in an oven at 37°C with periodic agitation. The analytical work was performed by a commercial laboratory. The results are tabulated in Table I.

Comparison of Predictions with Existing Workplace Limits

The data in Table I for the normal alkanes are plotted in Figure 2. Where a TLV exists, the specific point is plotted (for hexane, the TLV for "other isomers" is plotted, as the TLV for n-hexane is set on criteria other than narcosis and irritation). Where no TLV exists a vertical line is drawn at the appropriate value of the air/olive oil partition coefficient. This allows ready comparison of the potential of a given compound for formation of an atmosphere which is flammable, oxygen deficient, or narcosis inducing.

For example, take propane with an olive oil partition coefficient of 5.9. As the concentration in air increases (ascending the vertical line on Figure 2), first the LEL is encountered at a concentration of 21,200 ppm, then the line for narcosis onset is crossed at 47,000 ppm; finally, the line for displacement of oxygen at 140,000 ppm is reached. Clearly this model suggests that propane is not a simple asphyxiant; there will be physiological effects before displacement of oxygen below 18 percent occurs.

Indeed, this will be true for all materials having an air/olive oil partition coefficient greater than 1.6, the value at which the horizontal "18 percent oxygen in air" and the sloped "narcosis onset" lines intersect in Figure 2.

From Figure 2 the following conclusions can be drawn:

1. On the basis of narcosis, control as an asphyxiant (18% oxygen) is inadequate for butane and propane, marginal for ethane, but satisfactory for pure methane.
2. At a concentration of 100 percent of the LEL butane will be narcotic, but propane, ethane, and methane not so.

In addition, all of these hydrocarbons are expected to have

TABLE I. Partition Coefficients of Gases Between Olive Oil and Air at 37°C

Hydrocarbon	This Work*	Other References	Lower Explosive Limit (ppm) (from ref 15)	Predicted Onset of Narcosis (ppm) (from Figure 2)
Methane	0.89	0.31 (9)	50000	300000
Ethane	2.1		30000	130000
Ethylene	1.6	1.28 (11)	27500	170000
Acetylene	2.3	1.7 (9)	25000	120000
Propane	5.9		21200	47000
Propylene	6.0		20000	46000
Propyne	11			25000
Cyclo-propane	1.2	0.7 (11)	24000	24000
		1.12 (11)		
		1.05 (11)		
		1.15 (9)		
Butane	1.7		18600	17000
Iso butane	1.2		18000	24000
Cis 2-butene	2.5		17500	11000
2-Butyne	5.2			5500
1,3-Butadiene	1.8			16000
Pentane		4.7 (14)	14000	
Hexane	8.7	14.6 (14)	11800	
		15.5 (13)		
Heptane		45.2 (14)	11000	
		40.5 (13)		
Benzene	1.60	4.61 (9)	14000	
		4.92 (9)		
		4.65 (13)		
Toluene		13.80 (9)	12700	220
		14.71 (9)		
		10.56 (13)		

*Analysis performed by a commercial laboratory using the method of Sato and Nakajima, as described by Perbellini *et al.*[10]