

STUDIES ON THE FORMATION AND DECOMPOSITION OF ETHER PEROXIDES

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It is generally known that most mixtures of a flammable anesthetic agent such as ether with air or oxygen are readily ignited by an open flame or by an electric arc or spark. For all of the common anesthetic gas mixtures, the Bureau of Mines has determined flammability limits (1), ignition energies (2), and temperatures for spontaneous combustion (3, 4).

It has been suggested that ignition of anesthetic mixtures may also have occurred owing to excessive development of heat in a carbon dioxide absorber used during anesthesia, and may have been caused by the explosive decomposition of ether peroxide (5). Since this is largely speculative, this report is concerned with: (1) the temperature attained in an absorber owing to heat of reaction of carbon dioxide and soda lime, (2) the rate of formation of ether peroxide in a conventional vaporizer, and (3) the rate of decomposition of ether peroxide in the presence of soda lime.

EXPERIMENTAL PROCEDURE

Maximum Temperatures in a Soda Lime Absorber.—Various nitrogen-carbon dioxide mixtures, preheated and humidified by bubbling through a water-scrubber which was maintained at 40–45 C., were passed through Wilson indicator soda lime in a Heidbrink 9B absorber at the rate of 10 liters per minute. The temperature rise was deter-

TABLE I
MAXIMUM TEMPERATURES RECORDED IN A 9B ABSORBER, PASSING NITROGEN-CARBON DIOXIDE MIXTURES THROUGH WILSON SODA LIME.
AT 10 L./MINUTE

CO ₂ in N ₂ (per cent)	5	10	15	20
Temperature (degrees centigrade)	55	70	72	76

mined by means of eleven thermocouples placed randomly throughout the chamber containing the soda lime. The time required to reach the maximum temperature varied from five to twenty minutes depending upon the quantity of carbon dioxide in the gas mixture. The maximum temperatures observed are shown in table 1.

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TABLE 2

PERCENTAGES OF PEROXIDE IN ETHER DURING OPEN-BOTTLE STORAGE IN OXYGEN FOR 12.8 DAYS, AND DURING VAPORIZATION BY OXYGEN FOR 3.9 DAYS*

Time in days	Peroxide (as H ₂ O ₂) per cent		
	In bottle	In vaporizer	In condensate
.9		<.005	None
1.6		.006	None
1.8	<.005		
2.2		.011	None
2.9		.014	None
3.9		.014	None
5.8	.005		
7.8	.005		
12.8	.049		

These gas mixtures were passed through the soda lime until the thermocouples indicated a drop of temperature. At this point the nitrogen was shut off, and pure carbon dioxide was passed through the absorber at the rate of one liter per minute. A maximum temperature of 100 to 115 C. was then attained, in approximately five minutes.

Rate of Ether Peroxide Formation.—To determine the effect of open storage on peroxide formation, ether was allowed to stand in pure oxygen at room temperature in a loosely stoppered colorless bottle. Peroxide was determined volumetrically using an excess of standard solution of arsenious oxide. The excess arsenious oxide was titrated with standard iodine until the yellow iodine color appears (6). Column 1, table 2, shows the peroxide concentrations observed.

Oxygen was passed continuously through a Heidbrink 8 ether vaporizer at a rate of 250 ml./minute, set at "full open," and ether added periodically to replace the loss by evaporation. Columns 3 and 4, table 2, show the peroxide analysis of samples of the ether remaining in the vaporizer, and of the evaporated vapor as condensed in a Dry Ice trap.

Decomposition of Ether Peroxide by Soda Lime at Room Temperature.—Ten milliliters of ether containing 0.049 per cent of ether peroxide (calculated as H₂O₂) was shaken with two grams of soda lime for five minutes. Ether was then decanted and the soda lime extracted with four 20 ml. portions of anhydrous isopropyl alcohol. The combined ether and the extract was then analyzed and found to contain

TABLE 3

PERCENTAGES OF PEROXIDES REMAINING IN ETHER AFTER EXPOSURE TO SODA LIME, AND APPARENT CONSTANTS FOR RATE OF DECOMPOSITION

t (minutes)	P _t Peroxide (Per cent)	$K = \frac{2.3}{t} \log \frac{P_0 - P_t}{P_0 - P_1}$
0	.080 = P ₀	
1	.058	0.58
5	.047	0.22
15	.035	0.15
30	.030 = P ₃₀	

0.013 per cent peroxide or 26.5 per cent of the amount present originally. Similarly, a sample containing 0.014 per cent peroxide, after standing overnight in contact with soda lime, gave a negative test for peroxide.

To obtain data on the rate of decomposition, samples of ether containing 0.08 per cent peroxide (calculated as H_2O_2) were treated with soda lime for varying periods of time and the reaction rate constants, shown in table 3, were computed.

Reaction of Ether Peroxide and Soda Lime at Elevated Temperatures.—Although the experimental decomposition of ether peroxide by soda lime at room temperature, described above, would seem to deny the suggestion that hot soda lime could catalyze ether peroxide formation, there remained the suggestion that explosively rapid decomposition of ether peroxide might occur in the presence of soda lime.

To clarify this a Pyrex glass tube $2\frac{3}{8}$ inches (inside diameter) by 12 inches containing soda lime was heated electrically to 80–100 C. and gas mixtures containing ether were passed through it at a rate of

TABLE 4
COMPOSITION OF GAS MIXTURES PASSED THROUGH ELECTRICALLY
HEATED PYREX GLASS TUBE CONTAINING SODA LIME

	Oxygen (per cent)	Ether (per cent)	Carbon Dioxide (per cent)	Cyclopropane (per cent)
Mixture A	93.0	7.0	0	0
Mixture B	54.4	14.8	7.2	23.6
Mixture C	50.0	14.2	8.8	27.0

10 liters per minute. The ether was introduced into the gas stream from an electrically heated vaporizer and the gas mixtures were pre-heated and humidified by bubbling through water at 40 to 45 C. The exit gases were passed through two Dry Ice traps in series. Compositions of the gas mixtures used are shown in table 4.

At the end of an hour, the remaining ether in the vaporizer, the soda lime, and the condensed water and condensed ether were analyzed and all found to contain no measurable quantity of peroxide.

DISCUSSION

It is unlikely that the temperatures reached in a conventional soda lime absorber are sufficient for ignition of anesthetic mixtures. Even with pure carbon dioxide, a maximum soda lime temperature of 115 C. was observed, while the lowest ignition temperature for a flammable anesthetic mixture measured by the Bureau of Mines was 182 C., for ether and pure oxygen. Since the ignition temperatures for other mixtures, such as ether-air or cyclopropane-oxygen, are far higher, it

would appear that there is a very considerable margin against ignition. This is confirmed by the lack of explosive reaction when hot gases containing high percentages of carbon dioxide and ether were passed through hot soda lime.

Ether in a loosely stoppered bottle or in a vaporizer jar will accumulate peroxides very slowly initially, but then progressively faster. It is probably inadvisable to leave ether in a vaporizer more than two days, or in an unsealed bottle for over one week, since it is known that the peroxide residue left after evaporation of the ether may explode readily. The lower rate of formation in a partially closed bottle may be due to reduction of oxygen partial pressure by the ether vapor, as compared with a vaporizer with oxygen flowing.

The increasing rate of peroxide formation indicates an autocatalytic reaction, so that adding fresh ether to the residual ether in the jar appears undesirable over a period greater than two days. Since the peroxides are water soluble, rinsing a vaporizer wick and jar at two day intervals is indicated.

The suggestion that soda lime might catalyze the formation of peroxides appears erroneous. The rate of formation of peroxide appears so much slower than the rate of decomposition by soda lime that the suggested accumulation of peroxides in a soda lime container also appears impossible. On the other hand the rate of reduction of peroxides by soda lime is so slow that explosive decomposition of peroxides in the presence of soda lime appears impossible.

Contamination of other parts of a gas machine by peroxides appears very improbable. Condensate ether from a vaporizer showed no measurable peroxide, indicating that the peroxides are relatively much less volatile. Contamination by formation of ether peroxides in parts of the gas machine other than the vaporizer or soda lime chamber also seems improbable since no peroxides were observed in the condensate during the hot absorber tests, although these should have formed in the heated portions of the system past the soda lime if appreciable formation at room temperature were to be expected.

The reaction between soda lime and ether peroxide appears to be complex, rather than first-order, as indicated by the changing value of the rate constant K (table 3) when the data were substituted in the first-order equation. The literature (7) also indicates that the decomposition of peroxides in ether solution is a complex reaction, and generally follows a rate law such as:

$$-\frac{dP}{dt} = KP + K'P^2$$

where P is the peroxide content, t the time, K the first-order rate constant, K' the induced decomposition rate constant and x the induced order term.

SUMMARY AND CONCLUSIONS

The maximum temperatures attained owing to carbon dioxide absorption in a typical soda lime canister with anesthetic gas mixtures were found to be far below the published ignition temperatures for these mixtures.

It was found that heated anesthetic mixtures containing large amounts of carbon dioxide could safely be passed through soda lime heated far above its normal operating temperature. The initial rate of peroxide formation in diethyl ether is so slow under typical conditions that ether may probably be safely used in a vaporizer for two days or kept in a loosely stoppered bottle for one week. However, the rate of formation appears to increase with time, so that discarding of ether after these periods appears advisable.

It appears unlikely that soda lime can promote peroxide formation or that it can decompose peroxides sufficiently rapidly for ignition to occur. It is also apparent that progressive accumulation of peroxides in soda lime is impossible.

Ether peroxide formed in a typical vaporizer was not carried in detectable amounts to other parts of a typical anesthetic machine.

When usual anesthetic gas mixtures were employed for a reasonable length of time under excessively hot conditions no peroxides were found anywhere in the apparatus.

REFERENCES

1. Coward, H. F., and Jones, G. W.: Limits of Flammability of Gases and Vapors. Bureau of Mines Bulletin 503, 1952.
2. Guest, P. G., and others: Static Electricity in Hospital Operating Suites. Bureau of Mines Bulletin 520 (Jan.) 1952.
3. Jones, G. W., Kennedy, R. E., and Thomas, G. J.: Explosion Hazards of Combustible Anesthetics. Bureau of Mines Technical Paper 553.
4. Jones, G. W., Kennedy, R. E., and Thomas, G. J.: Explosive Properties of Cyclopropane. Bureau of Mines Report of Investigations 3511 (1940).
5. Weaver, E. R.: A Suggested Explanation for the Origin of Explosions in Anesthetic Machines. Bulletins of the U. S. Army Medical Department (March) 1949.
6. Siggia, S.: Determination of Benzoyl Peroxide in Organic Media. *Anal. Chem.* 19: 822 (1947).
7. Tobolsky, A. V., and Mesrobian, R. B.: Peroxides: Their Chemistry, Decomposition, and Role in Polymerization. New York, Interscience Publishers, Inc., 1954, pp. 75-83.