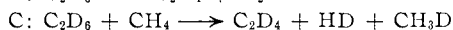
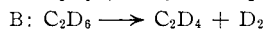
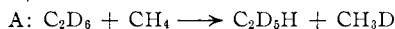


tion increases. The CD_3H concentration increases with increasing concentration of NO because CD_3H can be formed only in a non-chain radical reaction, it depends only on the initial split of the ethane- d_6 molecule and is independent of any chain. As the chain shortens with increasing concentration of NO , the initial split becomes more important and the concentration of CD_3H increases.

On the other hand, C_2D_5H is formed only in a chain-radical reaction. With addition of NO the chain becomes less important compared with the original split, and the concentration of C_2D_5H should fall. CH_3D can be formed either in a chain or non-chain radical reaction and its constancy with respect to increasing concentration of NO may be ascribed to a cancelling of two effects. The $(CH_3D + D_2)$ row is a measure of the accuracy of the experimental data. For every molecule of C_2D_6 decomposing by a chain, a molecule of either D_2 or CH_3D is formed. Since the $(CH_3D + D_2)$ values differ considerably from 100, our results are only semi-quantitative.⁶

(6) It was pointed out by the reviewer that the reactions designated as A, B and C are



As pointed out previously the CD_3H is a measure of the initial split of the C_2D_6 . The CH_3D can be formed in either a "non-chain" or a "chain radical" reaction. If we neglect the CH_3D formed outside of the chain, the ratio of CH_3D to CD_3H (Table III) is essentially the length of the chain consisting of reactions (6), (8) and (4). The experimental results indicate that, as nitric oxide is added, the chain length decreases from 25 to about 6 links. As the chain length decreases the initial split of the C_2D_6 and the "non-chain radical" reactions become relatively more important than in the uninhibited reaction. This seems to be confirmed by the fact that the amount of CD_3H formed increases as the nitric oxide concentration increases.

These results support the previously published conclusion that the thermal decomposition of C_2H_6 or C_2D_6 is a chain reaction in which there is negligible direct molecular separation of H_2 or D_2 .

Acknowledgment.—The authors wish to thank Dr. F. O. Rice who gave generously of his time and knowledge during the course of this work.

It is a consequence of this mechanism that

$$[C_2D_5H] = [CH_3D] - [HD]$$

It is seen from Table III that the data fit this relation at intermediate nitric oxide concentrations but deviate markedly at low and high concentrations.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Oxidation of Lower Paraffin Hydrocarbons. I. Room Temperature Reaction of Methane, Propane, *n*-Butane and Isobutane with Ozonized Oxygen¹

BY CLARENCE C. SCHUBERT, S. J., AND ROBERT N. PEASE

RECEIVED JANUARY 20, 1956

Reaction rates of ozonized oxygen (*ca.* 3 mole % O_3) with methane, propane, *n*-butane and isobutane were measured, *in situ*, in a temperature-controlled infrared absorption cell by observing the decrease of ozone concentration as measured by the absorption at 1055 cm.^{-1} . The activation energies calculated on the basis of a reaction first-order with respect to ozone were 14.9, 12.1, 11.1 and 10.3 kcal., respectively. The pre-exponential term for the methane-ozone reaction was found to be 7.2×10^{10} , for propane-ozone 3.1×10^9 , for *n*-butane-ozone 8.2×10^8 and for isobutane-ozone 4.4×10^8 cc. mole⁻¹ sec.⁻¹ estimated on the basis of a reaction rate $\propto [O_3][HC]$. The isobutane-ozone reaction was predominantly homogeneous; *n*-butane-ozone showed some acceleration in rate due to increased Pyrex surface, little dependence on sodium chloride surface. The main gaseous product of the isobutane-ozone reaction was *t*-butyl alcohol with smaller amounts of acetone and 1-carbon products approximately equal to molar amounts of acetone. A mechanism based on the postulation of a low lying triplet state of ozone is presented.

Relatively little work has been done on the kinetics of the action of ozone on saturated hydrocarbons. It was reported by Otto² in 1898 that ozone reacted with methane to yield aldehyde at temperatures as low as 15° . In 1922 Wheeler and Blair³ observed that at 100° methane reacted with ozone at such speed that 53% of the introduced

ozone disappeared within 2 minutes. Also in 1922 Elworthy⁴ concluded that the reaction of methane with ozone gave promise as a means to produce methanol and formaldehyde. In 1928 Riesenfeld and Gurian⁵ re-investigated this reaction.

Ethanol was reported⁶ to result from the action of ozone on ethane and this reaction was noted to proceed with greater rapidity than the reaction of ozone with methane. Some patents⁷ have been issued to cover the use of ozone as a stimulator for the combustion of gaseous, liquid or solid fuels.

(1) Taken from a thesis submitted by C. C. Schubert, S. J., in partial fulfillment of the requirements for the Ph.D. degree. The work described in this paper was supported jointly by Contract NOrd-7920 with the U. S. Naval Bureau of Ordnance as coordinated by the Applied Physics Laboratory, The Johns Hopkins University and by Contract N6-ori-105 with the Office of Naval Research as coordinated by Project Squid, Princeton University. Reproduction, translation, publication, use and disposal in whole or in part by or for the United States Government is permitted.

(2) M. M. Otto, *Ann. chim. phys.*, [VII] **13**, 109 (1898).

(3) T. S. Wheeler and E. W. Blair, *J. Chem. Soc. Ind.*, **41**, 303 (1922).

(4) R. T. Elworthy, *Trans. Roy. Soc. Can.*, [III] **16**, 93 (1922).

(5) E. H. Riesenfeld and D. Gurian, *Z. physik. Chem.*, **A139**, 169 (1928).

(6) W. A. Bone and J. Drugman, *Proc. Chem. Soc.*, **20**, 127 (1904).

(7) C. E. Thorpe, "Bibliography of Ozone Technology," Vol. I, Armour Research Corp., Ill. Inst. of Tech., Tech Center, Chicago, 1954.

In a study of the action of ozone on propane and a mixture of butanes, Briner⁸ showed that ozone will initiate a chain reaction at the temperature at which slow combustion occurs. He measured the ratio of oxygen fixed in product to oxygen added to the reaction mixture as ozone. This ratio, for an approximately equimolar mixture of butane and oxygen (plus *ca.* 0.6 mole % O₃) varied from 0.11 at 20°, 0.66 at 150°, to 5.36 at 290°. For propane the ratio was observed to be 1.14 at 260° and 1.38 at 300°.

This paper describes the experimental results obtained during the study of the reaction between ozonized oxygen (*ca.* 3 mole % O₃) and the paraffins methane, propane, *n*-butane and isobutane within the temperature range 25 to 50°. A subsequent paper describes in somewhat greater detail the results of experiments in the range from 110° up to the temperature at which the reaction merges into the normal slow combustion.

Experimental Method

Reaction was followed by observations made *in situ* on the infrared absorption of the reacting gases. For the purposes of this study special gas cells were constructed which were of 10 cm. length and provided with an outer jacket in which water was circulated at convenient constant temperatures. The cells, constructed of Pyrex, were equipped with sodium chloride windows sealed with glyptal to the Pyrex cell. These cells were the reaction vessels. A balancing cell filled with hydrocarbon and oxygen made it possible to record only the absorptions which pertained to the gaseous reaction products and to ozone. Absorptions due to the hydrocarbons were effectively cancelled out. The cells were used in conjunction with a Perkin-Elmer Model 21 recording spectrometer operated with a slit setting No. 925 and scanned at slow speeds when spectral regions of interest were being traversed.

The operations required in the course of a typical experiment were the following.

After having adjusted the spectrometer, the gas cells were flushed out and filled to one atm., the balancing cell first, then the reaction cell. The gas mixture was determined by flowmeter settings. After filling the balancing cell, the reaction cell was filled in the same setup with the identical flowmeter settings, but in this case the electrical switch controlling the Siemens-type ozonizer was thrown in order to ozonize the oxygen. This method assured the close balancing of the two cells. Matheson C.P. isobutane was found to have traces of isobutene, but these were satisfactorily removed by scrubbing with sulfuric acid. No purification procedures were required for the C.P. methane, propane or *n*-butane. American Oxygen Co. oxygen was dried over magnesium perchlorate before use.

Immediately after having passed the mixed gases through the reaction cell until it was thoroughly flushed with the reactants, the thermostat chamber of the cell was connected to the constant temperature water circulatory pump, final adjustments of the infrared spectrometer made with the cells in position, and then the first measurement was made of the ozone absorption at 1055 cm.⁻¹. The elapsed time between that of filling and the first ozone measurement was generally of the order of 3 minutes.

At the beginning of a run the absorptions caused by ozone were the only appreciable peaks. After the initial reading was made of the ozone absorption, the spectrometer was caused to scan the peaks of interest as often as was convenient.

In the experiments described below the gas mixtures were maintained at the following molar ratios

Mixture	Molar ratio hydrocarbon/oxygen
Methane-oxygen	1.00
Propane-oxygen	1.50
<i>n</i> -Butane-oxygen	1.85
Isobutane-oxygen	1.22

(8) E. Briner and J. Carceller, *Helv. Chim. Acta* **18**, 973 (1935).

Measurement of Concentrations.—The concentration of ozone was determined quantitatively during the course of an experiment by observing the absorption band at 1055 cm.⁻¹. A calibration chart of this absorption as a function of ozone concentration was prepared based on an absolute method found to be superior to the analytical method which employs potassium iodide. This has been described⁹ and is similar in principle to Jahn's¹⁰ method. It is based on the volume (or pressure) change resulting from the decomposition of ozone on a hot platinum filament. The concentration of hydrocarbon was effectively constant throughout the time of the experiments, due to the small concentration of the reactive ozone.

The reaction products which were analyzed quantitatively by the technique described above were the gaseous products or vapors: carbon dioxide, carbon monoxide, formic acid, acetone, methanol and (for isobutane) *t*-butyl alcohol. Small amounts of formaldehyde were known to be present at concentrations less than 0.016 mmole liter⁻¹ (0.3 mm) but were too small for quantitative detection by infrared absorption.

Carbon dioxide was estimated by means of a calibration chart prepared by filling a 10 cm. gas cell with carbon dioxide at various pressures in the range of interest, 0 to 10 mm. The extinction at 2300 cm.⁻¹ was measured at a total pressure of one atmosphere in all cases, the make-up gas being air.

Formic acid vapor was calibrated at 1120 and 1108 cm.⁻¹ with a sample of formic acid stated to be 99.8% pure. From the data of Coolidge,¹¹ at 1 mm. formic acid is 41% dimeric at 25°, about 26% dimeric at 37° and 15% dimeric at 50°. This enabled conversion of mm. Hg pressure to molar concentration units.

Methanol vapor was estimated from the height of the sharp absorption at 1034 cm.⁻¹. This absorption lies in the same position as one of the strong absorption bands of ozone, but by making a measurement by the base line method on the sharp absorption of the "q" branch of methanol's strongest absorption, a reasonable estimate could be obtained for the concentration of methanol.

Acetone was determined by means of its carbonyl absorption at 1740 cm.⁻¹. Because formic acid has a carbonyl absorption with a higher extinction coefficient than that of acetone, it was necessary to allow for the absorption caused by the former in calculating the concentration of acetone. Another determination of the value for the pressure of acetone was made by means of the acetone absorption at 1220 cm.⁻¹. At this frequency, correction had to be made for the amount of *t*-butyl alcohol (only in the case of isobutane). These two procedures gave concordant results for the concentrations of acetone and are probably correct to about 10%.

For the analysis of *t*-butyl alcohol vapor, the predominant product from isobutane, the frequency chosen for calibration purposes was 930 cm.⁻¹. The extinction at this frequency of a middle fraction of freshly distilled *t*-butyl alcohol was measured by filling a 10-cm. gas cell with various pressures of *t*-butyl alcohol vapor from 1 to 20 mm., then adding air to bring the total pressure to one atmosphere. The recording conditions were identical to those used while making a run with the hydrocarbon and ozonized oxygen.

Results

Representative determinations of product yields by infrared absorption *in situ* are given in Table I and for isobutane at 28.5° in Fig. 1. The only detected products containing more than one carbon atom were acetone from propane and isobutane and *t*-butyl alcohol from the latter. Formaldehyde was not detected (compare refs. 2, 4); and there was no carbon monoxide except from methane. The only other products present in substantial amounts were carbon dioxide from propane and *n*-butane and an unidentified substance from *n*-butane which absorbed strongly at 1170 and 1750

(9) C. C. Schubert and D. Garvin, to be published.

(10) S. Jahn, *Ber.*, **43**, 2319 (1910).

(11) A. S. Coolidge, *THIS JOURNAL*, **50**, 2166 (1928).

TABLE I

Hydro-carbon	Temp., °C.	MOLES OF PRODUCT PER MOLE OF OZONE CONSUMED						<i>t</i> -Butyl alc.	G. atoms O in prod.
		HCOOH	CO ₂	CO	CH ₃ OH	Acetone			
CH ₄	50	0.12	0.2	0.20	<0.02	0.83	
C ₃ H ₈	50	.13	.77	< .03	.02	0.42	..	2.24	
<i>n</i> -C ₄ H ₁₀	50	.20	.82	< .03	.05	2.09 ^a	
<i>i</i> -C ₄ H ₁₀	25.0	.02	.16	< .03	< .01	.23	0.68	1.31	
	28.5	.02	.17	< .03	< .01	.30	.80	1.49	
	37.5	.02	.24	< .03	.01	.34	.60	1.47	
	50.0	.03	.16	< .03	.03	.44	.75	1.60	

^a There was also produced a substance (perhaps a peracid) which absorbs at 1170 and 1750 cm.⁻¹

cm.⁻¹. The latter may have been a peracid.¹² No alcohols other than methanol and *t*-butyl alcohol were observed.

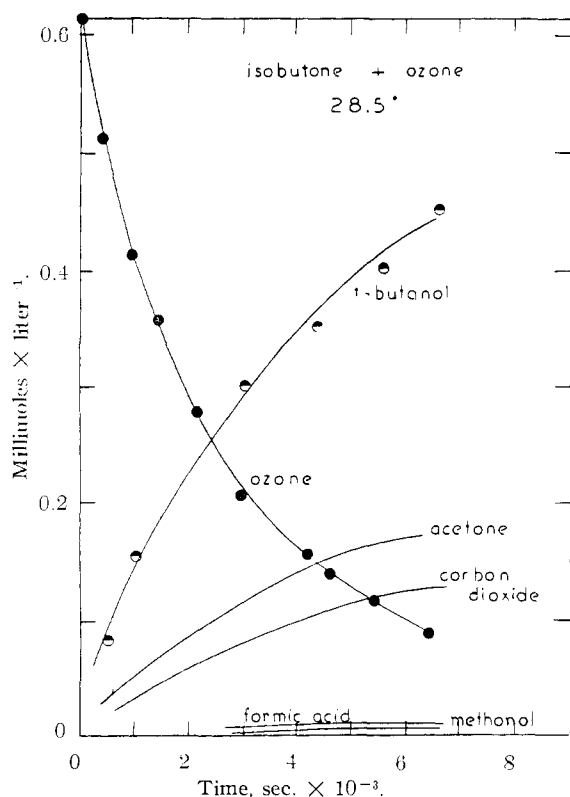


Fig. 1.—Gaseous phase reaction products from the reaction of isobutane (55 mole %) and ozonized oxygen (45 mole %) as determined from infrared spectra. Total pressure of reactants = 760 mm.

A typical experiment with isobutane conducted in the temperature controlled cells resulted in the information shown in Fig. 1. It is inferred from this experiment and others conducted at 25, 28.5, 37.5 and 50° that ozone reacts with isobutane to yield principally *t*-butyl alcohol and about 1/3 to 1/2 as much acetone throughout the temperature range 25–50°. Further, the sum of the molar quantities of one-carbon products, methanol, carbon dioxide and formic acid approached the molar amount of acetone generated. It will be noted that the sum of *t*-butyl alcohol and acetone was roughly equivalent to the ozone reacted.

(12) P. L. Hanst, E. R. Stephens and Wm. Scott, paper presented during 20th Midyear Meeting of the American Petroleum Inst. Div. of Refining, St. Louis, Mo., May 10, 1955.

In order to determine whether acetone, formic acid and carbon dioxide resulted from the secondary reaction of *t*-butyl alcohol with ozone, an experiment was conducted in which 22 mm. of *t*-butyl alcohol was added to the reaction mixture. There resulted neither an increase in the rate of loss of ozone nor production of more acetone than in the runs conducted without added *t*-butyl alcohol. It is thus indicated that the substances in question are formed directly. This is consistent with the shapes of the curves in Fig. 1.

Formaldehyde was detected qualitatively in the isobutane reaction in a 1-meter absorption tube, observing the characteristic ultraviolet absorption bands by means of a Warren Spectracord in conjunction with a Beckman DU spectrometer. However, the amount present was insufficient to produce any noticeable infrared absorption in the 10-cm. cells. It would have been possible to identify readily as little as 0.3 mm. of formaldehyde by means of its distinctively shaped carbonyl absorption.

The rate dependence on ozone concentration for the reaction of methane, propane, *n*-butane and isobutane with ozonized oxygen was shown to be first order with respect to ozone by plotting the logarithm of the ozone concentration against time. Linear plots were obtained such as are shown for the case of isobutane at four temperatures, Fig. 2, and for methane, propane and the butanes at one temperature, Fig. 3. Departures from linearity occurred only toward the end of the reaction when product absorptions interfered with the reliability of the value of the ozone concentration determination.

Surface effects were investigated as follows. Since the reactor was composed of a Pyrex body with sodium chloride windows it was necessary to study the effect of increased Pyrex and salt surfaces independently. To this end a cell was modified by the addition of a concentric Pyrex tube of such surface area that the Pyrex surface to volume ratio was changed from 1.48 to 4.34 cm.⁻¹. The Pyrex tube was situated in the cell so as to allow free passage of the infrared light beam. In another cell were placed sodium chloride crystals of measured size to change the sodium chloride surface to volume ratio from 0.247 to 1.26 cm.⁻¹, a five-fold increase.

Results are given in Table II in terms of a first-order constant based on ozone consumption, the hydrocarbon concentration being taken as constant. It is evident that the isobutane reaction is substantially independent of surface. On the other

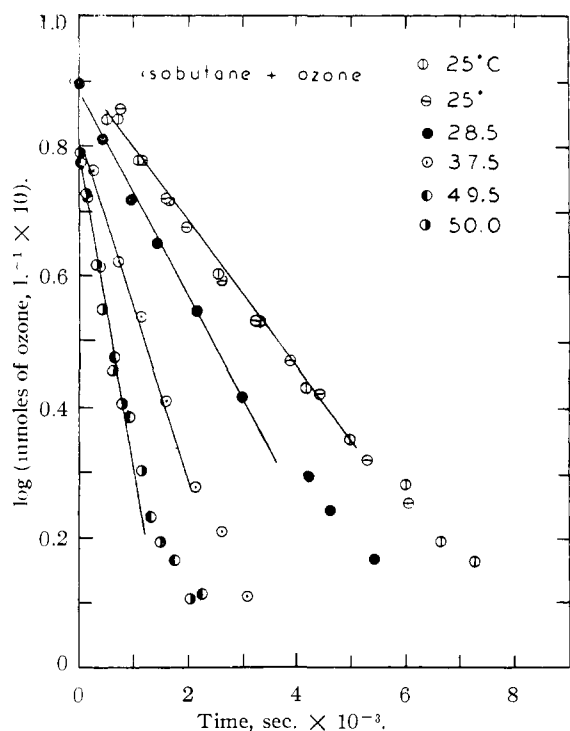


Fig. 2.—Decrease of \log_{10} concentration of ozone vs. time for a mixture of 55 mole % isobutane and 45 mole % ozonized oxygen.

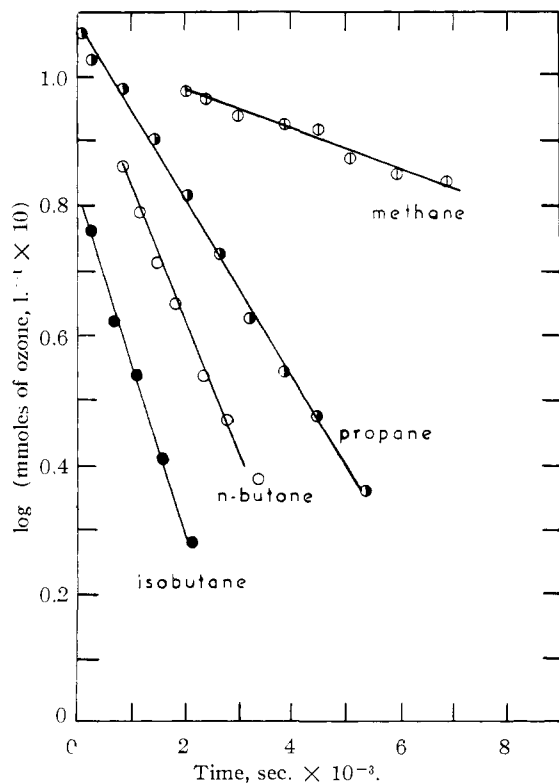


Fig. 3.—First-order plots for the reaction of ozonized oxygen with methane and propane at 39.5°, *n*-butane and isobutane at 37.5°.

hand, the *n*-butane reaction is definitely faster with added surface (Pyrex or NaCl). An estimate

of the surface contribution in the standard runs (no added surface) indicates that this amounts to about 20% of the total.

TABLE II
EFFECT OF SURFACE ON THE HYDROCARBON-OZONE REACTION AT 28.5°

Surface-volume ratio, cm. ⁻¹ Pyrex	NaCl	$k \times 10^4$, ^a sec. ⁻¹
Isobutane-ozone reaction		
4.34	0.27	3.5
1.48	0.247	3.7
1.60	1.26	3.3
<i>n</i> -Butane-ozone reaction		
4.34	0.27	3.3
1.48	0.247	2.5
1.60	1.26	2.6

^a Based on ozone consumption, hydrocarbon concentration being considered as constant. Values of k are averages of 2 or 3 runs.

The effect of temperature on the rates of the hydrocarbon-ozone reaction is shown graphically in an Arrhenius plot of $\log k$ vs. $1/T$ (Fig. 4).

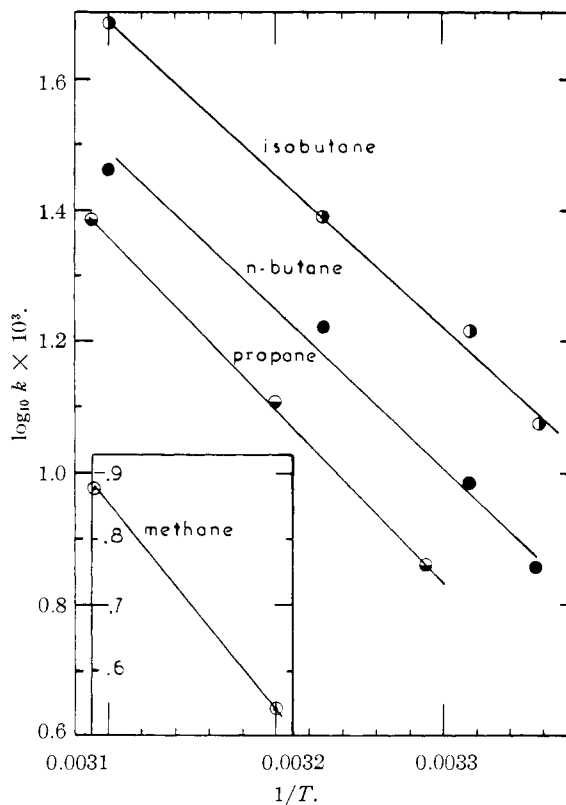


Fig. 4.—Arrhenius plots for paraffin-ozonized oxygen reactions.

The rate constants in this case are calculated on the basis of a second-order reaction

$$-d[O_3]/dt = k[O_3][HC]$$

where k has the units, l. moles⁻¹ sec.⁻¹. Data were obtained from plots such as those of Figs. 2 and 3, with conversion to the new units, taking the concentration of hydrocarbon as constant through each run.

The Arrhenius constants, A and E^* from the equation

$$k = A \exp. -E^*/RT \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$

are given in Table III. It will be noted that the A factors are in the "normal" range for bimolecular reactions between complex molecules¹³ for the units involved. This is in contrast to the results of Cadle and Schadt¹⁴ on the corresponding reactions of ethylene and acetylene, for which quite low A factors were calculated, 1.2×10^8 and 1.9×10^6 cc. mole⁻¹ sec.⁻¹, respectively.

TABLE III
VALUES OF A AND E^* FOR THE HYDROCARBON-OZONE REACTIONS

H.C.	A , cc. mole ⁻¹ sec. ⁻¹	E^* , ^a kcal. mole ⁻¹	k_{25} (calcd.), cc. mole ⁻¹ sec. ⁻¹
CH ₄	7.2×10^{10}	14.9	0.85
C ₃ H ₈	3.1×10^9	12.1	4.1
<i>n</i> -C ₄ H ₁₀	8.2×10^8	11.1	5.9
<i>i</i> -C ₄ H ₁₀	4.4×10^8	10.3	12.2
C ₂ H ₄ ^a	1.9×10^6	0	1.9×10^6
C ₂ H ₂ ^a	1.2×10^8	4.8	3.6×10^4

^a Data of Cadle and Schadt, ref. 14.

Discussion

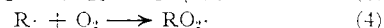
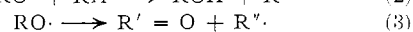
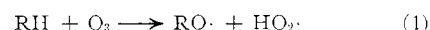
The reaction of ozone with paraffins proceeds with a relatively low energy of activation. Perhaps this low value should be associated with the reaction of a triplet low lying excited electronic state of the ozone molecule, normally in a ¹Σ state,¹⁵

(13) A. A. Frost and R. G. Pearson, "Kinetics," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 92.

(14) R. D. Cadle and S. Schadt, THIS JOURNAL, **74**, 6002 (1952); *J. Chem. Phys.*, **21**, 163 (1953), and private communication. The infrared absorption method was employed.

(15) R. Trambarulo, S. Ghosh, C. Burrus, Jr., and W. Gordy, *J. Chem. Phys.*, **21**, 851 (1953).

with hydrocarbon in the series of reactions



The principal difference between the mode of reaction of normal paraffins relative to that of a branched paraffin like isobutane would then reside in the relative stability of the alkoxy radicals, RO₂·. In the case of isobutane, *t*-butoxy radical is sufficiently stable under the reaction conditions to yield, by hydrogen abstraction from RH, *t*-butyl alcohol. With *n*-butane and propane the notable absence of alcohols other than methanol is an indication that this reaction (2) is of minor importance. Acetone results from propane by the ejection of a hydrogen atom from the isopropoxy radical, from isobutane by the ejection of a methyl radical from the *t*-butoxy radical (reaction 3). An alternate splitting of the isopropoxy radical to acetaldehyde plus a methyl radical probably occurs with the subsequent rapid oxidation of acetaldehyde.

It is to be noted that in the temperature region investigated, 25–50°, the order of reactivity is that which would be expected on the basis of the strengths of the C–H bonds involved. Isobutane–ozone has a lower activation energy than *n*-butane–ozone. The ease with which the tertiary hydrogen may be withdrawn from isobutane may, in turn, account in some measure for the greater stability of the *t*-butoxy radical.

At low temperatures it is to be presumed that HO₂· and RO₂· are relatively inert radicals and are neutralized by recombination at the walls of the reactor. Under these conditions the over-all reaction would be second order as assumed.

PRINCETON, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF CONNECTICUT]

The Kinetics of the Thermal Decomposition of Gaseous Diethyl Ketone

BY CHAS. E. WARING AND C. S. BARLOW¹

RECEIVED NOVEMBER 23, 1955

The kinetics of the thermal decomposition of diethyl ketone indicates that the reaction proceeds through a chain mechanism. In contrast to the thermal decomposition of acetone and methyl ethyl ketone, nitric oxide inhibits, rather than catalyzes, this reaction. Propylene also inhibits the rate of decomposition of diethyl ketone, but much more propylene than nitric oxide is required to reduce the rate to a limiting value. Analyses of the products of reaction at various time intervals have been made and these are compared with analyses made on the inhibited reactions. A reaction mechanism is proposed to account for the observed experimental facts.

Introduction

Studies of the kinetics of the thermal decomposition of acetone^{2,3} and of methyl ethyl ketone^{4,5} revealed interesting similarities. Both are markedly catalyzed by nitric oxide but the rates of decomposition of each are reduced to a limiting value in the presence of propylene. This latter effect has

(1) Presented in partial fulfillment of the requirements for the Ph. D. degree at the University of Connecticut, 1951.

(2) C. A. Winkler and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A149**, 340 (1935).

(3) R. E. Smith and C. N. Hinshelwood, *ibid.*, **A183**, 33 (1944).

(4) C. E. Waring and W. E. Mutter, THIS JOURNAL, **70**, 4073 (1948).

(5) C. E. Waring and M. Spector, *ibid.*, **77**, 6453 (1955).

been taken as evidence that both decompositions proceed through a chain mechanism. The catalytic effect of nitric oxide, on the other hand, has been attributed to its reaction with the ketenes, present in the reaction products, to produce oxidation products.

The activation energies of acetone and methyl ethyl ketone were found to be essentially identical, namely, 68.0 and 67.2 kcal., respectively. This, together with the fact that the only saturated hydrocarbon found in the reaction product of either ketone was methane, was taken as evidence that the initial bond rupture in the decomposition of