2-Phenyl-2-cycloheptenone (Va).—A 53.5-g. (0.5 mole) sample of benzaldehyde was carried through the sequence described above but with the following additions to the procedure. The crude product from the first distillation was refluxed for 2 hours with 50 ml. of benzene and 20 ml. of concentrated hydrochloric acid (to remove dibenzalhydrazine), and the benzene layer was then separated, washed with water, and evaporated. The resulting material was treated with 15.8 g. (0.2 mole) of pyridine and refluxed for 3 hours. The residue remaining after the usual processing was distilled through a 4-inch Vigreux column to give 22 g. (24% over-all from benzaldehyde) of a pale yellow oil, b.p. 128–133° (1 mm.), $n^{25}\text{D}$ 1.5745. The carbon analysis of this material was *ca.* 1.5% low even after careful redistillation. It was necessary, therefore, to prepare a pure sample *via* the semicarbazone which, upon decomposition, yielded a colorless oil, $n^{25}\text{D}$ 1.5712 (reported[16] $n^{11}\text{D}$ 1.5720), $\bar{\nu}_{\max}^{\text{liq}}$ 1680 cm.$^{-1}$ for C=O.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.81; H, 7.39.

The semicarbazone of Va was obtained as colorless plates, m.p. 178–179° (reported[14] 180–181°).

Hydrogenation of Va in the presence of 5% palladium-on-charcoal in ethyl acetate yielded 2-phenylcycloheptanone (IVa), identified by comparison with authentic material.

2,3,4-Trimethoxybenzaldehyde (Ih) was conveniently prepared on a large scale by a method patterned after that of Sommers, *et al.*[26] A 130-g. sample of 1,2,3-trimethoxybenzene was added to a mixture of 168 g. of phosphorus oxychloride and 144 g. of N-methylformanilide over a period of 2.5 hours. After stirring for an additional 3 hours, the reaction mixture was poured into 2 l. of ice-water and allowed to stand overnight. The product was then extracted into ether and the ether solution was treated with saturated sodium bisulfite solution. The bisulfite product was separated, washed with ether, and decomposed to yield 96 g. (64%) of Ih as a pale yellow oil, b.p. 121–124° (0.5 mm.). A 2,4-dinitrophenylhydrazone prepared from this product showed no depression in m.p. when admixed with a sample prepared by an alternate and unequivocal route.

[26] A. H. Sommers, R. J. Michaels and A. W. Weston, THIS JOURNAL, **74**, 5546 (1952).

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE GEORGE WASHINGTON UNIVERSITY]

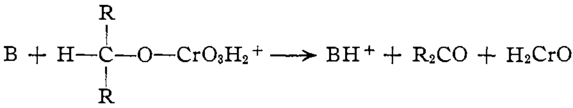
Oxidation of Triethylmethane and Other Hydrocarbons by Acidified Dichromate

BY W. F. SAGER AND ARTHUR BRADLEY[1]

RECEIVED AUGUST 24, 1954

Oxidation of triethylmethane by sodium dichromate in acidified aqueous acetic acid is shown to proceed through triethylcarbinol as the initial oxidation product. Evidence is presented which supports the view that hydrocarbon oxidations by this reagent result from electrophilic attack of the oxidant on the hydrocarbon to yield a carbonium ion.

This study was undertaken to identify the sequence of events which lead to the formation of ketones by oxidation of branched chain hydrocarbons with dichromate. The work reported here includes preliminary studies on the composition of the reaction mixture throughout the course of the oxidation and a more detailed analysis of the initial step. Identification of the means by which such a saturated system engages the oxidant is of special interest inasmuch as the esterification mechanism preferred by Westheimer and co-workers[2–5] for the oxidation of secondary alcohols cannot be paralleled. These authors demonstrated, in an exceptionally thorough investigation, that the transition state concentration was proportional to the alcohol, $HCrO_4^-$ and the square of the hydrogen ion concentration. Moreover, a study of deuteropropanol indicated that the hydrogen attached to the carbinol carbon is involved in the rate-determining step.[3] Finally, induced oxidation of the manganous ion showed the presence of tetravalent chromium in the reaction mixture.[5] This evidence was used to support the idea that chromium is reduced from a valence of six to four in an oxidation process which involves a base-initiated breakdown of a chromate ester.



$$B + H-\underset{R}{\overset{R}{C}}-O-CrO_3H_2^+ \longrightarrow BH^+ + R_2CO + H_2CrO_3$$

The lack of influence of oxygen[4,6] on chromic acid oxidations supports this conclusion.

Our approach to the similar questions connected with hydrocarbon oxidation followed three general lines: study of the reaction products, isotope effect on oxidation rate and effect of special structural features on the ease of C–H bond rupture. All studies concerned oxidations by sodium dichromate in aqueous acetic acid acidified with sulfuric acid, a useful agent for hydrocarbon oxidations. A general idea of the composition of the reaction mixture at various times was gained by analysis for ketone and dichromate. The other species, unreacted hydrocarbon, triethylcarbinol and propionic acid, could then be calculated, as indicated in the Experimental section, with the aid of the independently determined oxidation rate of triethylcarbinol and 3-pentanone. An analysis by fractional distillation for all components except the acid was used as a check on the other analytical results. Similar measurements were made on the oxidation of triethyldeuteromethane. Last of all the behavior of bicyclic systems was studied by measurements on the oxidation rate of camphane and the nature of its oxidation product.

Discussion

By the means mentioned previously the primary oxidation product of triethylmethane is clearly triethylcarbinol (Fig. 2). Moreover, these results were checked by a larger scale run of short duration which was analyzed by fractional distillation. It yielded 9% of unreacted hydrocarbon, 41% carbinol and 36% ketone.

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[1] Office of Naval Research Fellow, 1952–1953.

[2] F. Holloway, M. Cohen and F. H. Westheimer, THIS JOURNAL, **73**, 65 (1951).

[3] F. H. Westheimer and N. Nicolaides, *ibid.*, **71**, 25 (1949).

[4] F. H. Westheimer and W. Watanabe, *J. Chem. Phys.*, **17**, 61 (1949).

[5] F. H. Westheimer and A. Novick, *ibid.*, **11**, 506 (1943).

[6] L. F. Fieser, THIS JOURNAL, **70**, 3237 (1948).

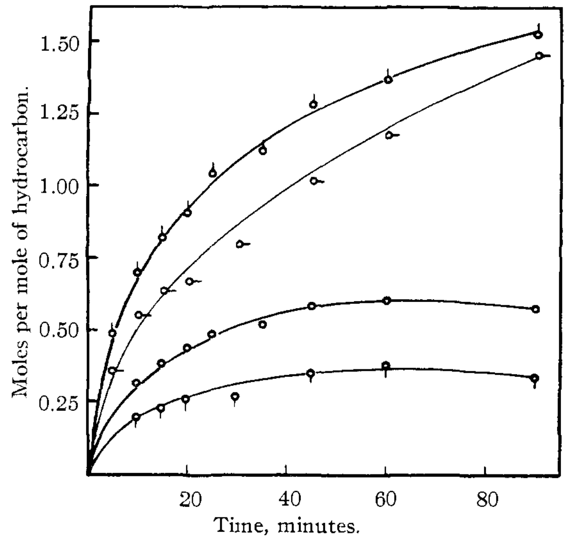

Fig. 1.—Effect of deuterium substitution on the oxidation rate: ó, triethylmethane (disappearance of dichromate); o-, deuterotriethylmethane (disappearance of dichromate); O, triethylmethane (appearance of pentanone-3); ♀, deuterotriethylmethane (appearance of pentanone-3).

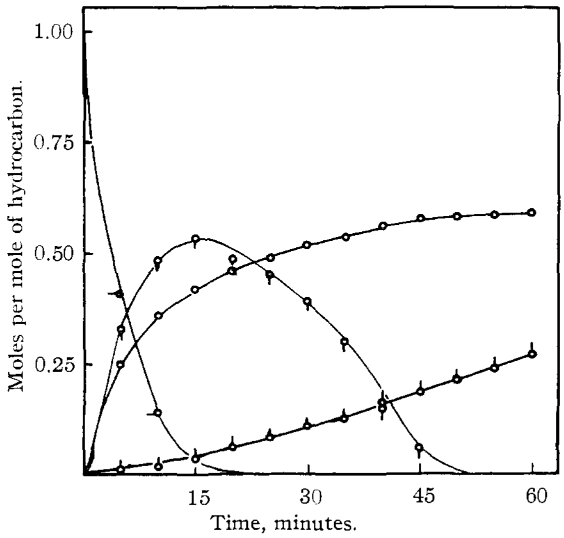

Fig. 2.—Time variation of triethylmethane oxidation products: O, pentanone-3; ó, propionic acid; ♀, triethylcarbinol; -o, triethylmethane.

Involvement of the tertiary carbon–hydrogen bond is suggested by the nature of the product and the isotope effect on the rate of oxidation observed when the tertiary hydrogen is replaced by deuterium. Quantitative analysis of the isotope effect was rendered very difficult by the various concurrent processes. However, it can be seen from Fig. 1 that the more rapid consumption of dichromate in initial stages of the oxidation of the normal compound, as well as the somewhat more rapid production of ketone, leaves no doubt as to the existence of a retardation of usual magnitude.

These results may be interpreted on the basis of a simple removal of the tertiary hydrogen atom or as removal of a molecule of hydrogen (dehydrogenation) to yield an olefin. The direct dehydrogenation to 3-ethylpentene-2 is eliminated as an important process by the observation that the olefin is immediately consumed by the oxidant and gives about a 40% yield of pentanone-3. No *t*-alcohol is formed in this process. The conclusion that oxidation proceeds much faster than solvolysis of the olefin, which these results suggest, was corroborated by the observation that the yield of ketone is almost independent of oxidant concentration. It is clear then that the rate of dichromate consumption and the amounts of triethylcarbinol and ketone found at various times can be accounted for on the basis that the first intermediate is the tertiary alcohol. Were an olefin the first intermediate, there is no way to account for the triethylcarbinol which was isolated in sizable amount at any early stage of the reaction.

A separate study of the behavior of triethylcarbinol gave results in excellent accord with the idea that this alcohol results from the first step of the process. Oxidation under the usual conditions showed that the concentration of ketone at various times and consumption of dichromate were very similar to those from the hydrocarbon oxidation and that the differences, most pronounced at the beginning of the run, were in the direction expected from this hypothesis.

The oxidation of bicyclic systems presents a complicated problem. Hydrocarbons such as camphane which bear a *t*-hydrogen at a bridgehead should be resistant to attack at this site by any of the mechanisms proposed. Nevertheless, both camphane and norcamphane are readily attacked under the conditions of our other oxidations. Epicamphor was isolated from the camphane oxidation. It would appear, then, that the facile oxidation reflects activation of the methylene group, a feature often observed in such bicyclic systems. An analogous oxidation of bornyl chloride to 8-chloroepicamphor has been observed.[7] In lieu of information on solvolysis rates in the epicamphor series, no reason for the particular site of attack can be put forward with confidence.

Little can be said of the mechanism of subsequent steps in production of the final products. Certainly the ease with which the olefin is cleaved by the oxidizing mixture admits its operation as the intermediate in degradation of the tertiary alcohol. There is also no doubt that this degradation, whatever the mechanism, is the slowest process in conversion of a *t*-hydrocarbon to a ketone.

Experimental

Chemicals.—Eastman Kodak Co. research grade 3-pentanone was used for calibration of the analytical method and in kinetic runs. The triethylcarbinol was prepared in the graduate synthetic organic laboratory course and had a boiling range of 142–143°. The 3-ethylpentane was obtained from the National Bureau of Standards. Sodium dichromate, manganous sulfate, ferrous ammonium sulfate, sulfuric acid, propionic acid and acetic acid were of reagent grade.

3-Ethyl-2-pentene.[8]—Eight grams of triethylcarbinol was refluxed with a small crystal of iodine for an hour and then distilled. The distillate, boiling from 55 to 80° consisted of a mixture of 3-ethyl-2-pentene and water. The olefin was

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[7] U. Bredt and P. Pinten, *J. prakt. Chem.*, [2] **115**, 48 (1927).

[8] J. Church, with F. Whitmore and R. McGrew, THIS JOURNAL, **56**, 176 (1934).

separated, dried over calcium chloride and redistilled. The material used boiled at 95°, n^{25}_D 1.4132 (reported[8] n^{20}_D 1.4142), yield 5.5 g. (80%).

Camphane.—Camphane was prepared through reduction of camphor by the Huang-Minlon modification[9] of the Wolff–Kishner reduction; yield 60%, m.p. 157–159°.

3-Deutero-3-ethylpentane.—Triethylcarbinylmagnesium chloride was prepared from 3.0 g. of magnesium turnings and 3.7 g. (0.028 mole) of 3-chloro-3-ethylpentane. The Grignard complex was hydrolyzed by slowly adding a solution of 2 g. of 99.75% deuterium oxide and 2 g. of acetyl chloride in 20 cc. of dry ether. To ensure complete destruction of the Grignard reagent about 25 g. of powdered Dry Ice was added and allowed to evaporate. The product was taken up in 100 cc. of ether, decanted from the excess magnesium and washed several times with water. It was then treated with small portions of 1% bromine in dichloromethane until a red color persisted. The excess bromine was destroyed with a few cc. of sodium thiosulfate solution and the solution washed thoroughly with water, dried over calcium chloride and distilled.

The ether–dichloromethane solution was filtered and distilled. When the boiling point had risen to above 50° the pressure was reduced to 25 mm. and with the pot at room temperature the next fraction (hydrocarbon) distilled into a Dry Ice–acetone trap. The residue, consisting of brominated products, was discarded. The bulk of this material was redistilled at atmospheric pressure, and 1.1 cc. (0.8 g., 0.008 mole, 28%) of liquid boiling at 91–93° was obtained. It showed no unsaturation, and underwent oxidation at a rate significantly slower than the normal 3-ethylpentane.

Oxidation Procedure.—The chromic acid mixture consisted of 5 cc. of 2 *N* aqueous sodium dichromate (296 g. dissolved in 500 ml.), 5 cc. of sulfuric acid and 45 cc. of acetic acid. This acid strength and dichromate concentration gave a convenient rate of oxidation for most of the compounds to be tested, and was used throughout. The materials were pipetted into 50 cc. of the mixture at 12°, at which temperature all rates were measured. The mole ratio of oxidant to substrate was approximately 8 in the various runs. Triethylcarbinol and 3-ethylpentene-2 were added in part of the acetic acid, although the final mixture was the same as described above. The curve for triethylcarbinol was very similar to that of 3-ethylpentane shown in Fig. 1. An experiment in which 3-ethylpentene-2 was added to the oxidation mixture and worked up after 15 seconds at 10° gave 40% 3-pentanone as measured by the optical method described below.

Method of Analysis for 3-Pentanone.—The ketone, although somewhat soluble in aqueous acetic acid, could be nearly quantitatively extracted by shaking with an equal volume of carbon tetrachloride. The method, which utilized the orange color of 3-pentanone 2,4-dinitrophenylhydrazone, was strictly empirical and consistent results were obtained only by rigidly adhering to a well-defined procedure. The conditions under which the samples were prepared were suggested by previous workers[10,11] and modified by preliminary experiments.

Each reading was the average of two duplicate measurements, taken on a pair of aliquots withdrawn from the oxidizing mixture at essentially the same time. Each 5-cc. aliquot was introduced into a mixture of 10 cc. of water and 15 cc. of carbon tetrachloride, the dilution of the chromic acid solution serving to quench the reaction. The container, which had a capacity of about 40 cc., was tightly stoppered and shaken for one minute, after which the layers were allowed to separate and most of the aqueous part was removed. The organic part was shaken for about 30 seconds with another 10 cc. of water. After the mixture had separated, again a 10-cc. aliquot of the organic layer was transferred to a clean container of the same size as the first. A 5-cc. portion of a solution of 0.500 g. of 2,4-dinitrophenylhydrazine in 1.0 *N* hydrochloric acid solution was added, the flask tightly stoppered and agitated vigorously for exactly five minutes. It was found that the time of shaking was very critical. After shaking, the organic layer was washed with 10 cc. of water. This last washing could be omitted or repeated without seriously affecting the reading on the Beckman spectrophotometer. Absorption of light of 420 mμ was measured. All readings were made with a slit width of 0.8, using a type of plastic absorption cell made especially for the instrument. The results were discarded if the pair of samples did not agree within 10% of each other, but ordinarily the discrepancy was less than half of this.

A great number of samples of this ketone were submitted to the analysis described above to calibrate the method. Weights of ketone were used so that a 5-cc. aliquot of oxidation mixture (usually 50 cc.) would contain 2 to 12 mg. at zero time. It was found first that a direct proportion existed between weight of ketone and optical density (Beer's law). The chromic acid, to which no ketone was added, gave blanks of 0.15 to 0.18, which were subtracted from subsequent readings in the same series. A net optical density of 0.10 was found to correspond to a concentration of 2 g. of ketone per liter of oxidation mixture. It was readily observed that the ketone was unstable in the oxidizing mixture, since successive aliquots showed diminishing absorption in the instrument.

Measurements of volumes and weights were well within the precision of this method, as were the slight variations in successive readings on the same sample of optical density. The significant errors undoubtedly stemmed from the mechanical manipulation involved in preparing the samples, such as separation of layers and shaking. Another cause of error, which was not appreciated at first, was the varying absorption of the plastic cells used with the spectrophotometer. It appeared that these cells were attacked by the solutions used. They were checked against each other from time to time and discarded when necessary.

The values plotted in Fig. 1 for 3-ethylpentane were reproduced to within 2% by duplicate measurements. The failure of certain kinetic runs to conform to the average was probably due to the crude temperature control (± 1°). No attempt was made to provide a really effective constant temperature bath in view of the exploratory nature of this work.

Analysis for Dichromate.—A Fischer titrimeter, fitted with a platinum–tungsten stirrer electrode was used to measure the change of dichromate concentration during the course of the oxidation experiments. A 5-cc. aliquot of the oxidation mixture was diluted to about 75 cc. with water and titrated with 0.500 *M* ferrous ammonium sulfate solution (98.0 g. dissolved in water containing 1 cc. of sulfuric acid and diluted to 500 ml.).

Oxidation of 3-Ethylpentane.—Most oxidations of this hydrocarbon were conducted by the procedure described earlier. In order to obtain a more detailed knowledge of the nature of the products the analytical results were analyzed in the following fashion. From the initial slope for the oxidation of 3-pentanone the rate constant for its disappearance was determined to be 0.012 min.$^{-1}$ under the usual conditions. In view of the large excess of oxidant, acid and water, one may assume that the rate follows approximately first-order kinetics and it was upon this basis that the above constant was calculated. The possibility that induced oxidation might interfere with this simple interpretation was rendered unlikely by investigation of the effect of manganous ion as described later. From this rate constant the amount of propionic acid was calculated by graphical integration of the ketone curve on the assumption that the ketone is cleanly cleaved to propionic and acetic acids. In support of this assumption is the observation that the oxidation proceeds without formation of water-insoluble products or gas. The difference between the amount of oxidant required to form these products and the amount actually consumed could then be used to calculate the amount of carbinol produced according to the equation

$$\text{Moles oxidant consumed} = 1/3 \text{ carbinol} - 4/3 \text{ ketone} - 7/3 \text{ propionic acid}$$

The amount of hydrocarbon was obtained by difference.

Time, min.	Mole per cent. of original hydrocarbon 3-Ethylpentane	Triethylcarbinol	3-Pentanone	Propionic acid
5	41	33	25	1
10	14	48	36	2
15	0	54	42	4
20	0	48	46	6
25	..	45	49	8

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[9] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[10] P. Shore, Master's Thesis, The George Washington University, 1952.

[11] L. Greenberg and D. Lester, *J. Biol. Chem.*, **154**, 177 (1944).

Time, min.	Mole per cent. of original hydrocarbon 3-Ethylpentane	Triethylcarbinol	3-Pentanone	Propionic acid
30	..	39	52	11
35	..	30	54	13
40	..	15	56	16
45	..	6	58	18
50	..		59	21
55	..		59	24
60	..		60	27

In order to obtain some check on this indirect method a larger scale oxidation was carried out and the mixture analyzed at an early stage by fractional distillation. A mixture of 50 cc. of 2 *N* aqueous sodium dichromate, 50 cc. of sulfuric acid and 450 cc. of glacial acetic acid was cooled to 8°. 3-Ethylpentane (5.0 g., 0.050 mole) was added and the mixture immersed in a cold water-bath and stirred for ten minutes during which time the temperature rose to 14°. The reaction was stopped after 10 minutes by adding about 300 g. of ice at once and 85 g. of sodium carbonate as fast as evolution of carbon dioxide would permit. After standing at room temperature overnight the solution was filtered from precipitated sodium sulfate, and both solid and filtrate were extracted several times with methylene chloride. The combined extracts (600 cc.) were washed with water and the solvent removed by fractionation. When the volume of product and solvent was reduced to 25 cc., 2 cc. of nitrobenzene was added and distillation continued on a concentric tube column. The following fractions were collected: 92–94°, 0.65 cc.; 102–104°,[12] 1.9 cc.; 141–143, 2.8 cc.

An infrared spectrum of the fraction boiling from 141 to 143°, except for a small carbonyl peak at 5.85 μ, was identical with that for an authentic sample of triethylcarbinol.

To check the possibility of induced oxidation, 84 mg. of $MnSO_4$ was added to the aqueous dichromate solution prior to mixture with the remaining reagents. The oxidation rate for 90 minutes was the same within experimental error as that for mixtures without added manganous ion.

Oxidation of Triethylcarbinol.—The oxidation of 0.270 g. of alcohol was carried out by the usual procedure. Analysis for consumption of dichromate at different times gave the following data.

Time, min.	Mole Cr_2O_7 per mole alcohol	Mole ketone per mole alcohol	Time, min.	Moles Cr_2O_7 per mole alcohol	Mole ketone per mole alcohol
0	0	0	20	0.48	0.35
2	0.05	0.08	30	.65	.46
3	.11		45	.90	.53
5	.20	.15	60	1.09	.60
10	.27	.24	75	1.18	.64
15	.38	.32	90	1.27	

Oxidation of Camphane.—An oxidation mixture consisting of 20 cc. of sulfuric acid, 180 cc. of acetic acid and 20 cc. of 2 *N* sodium dichromate was cooled to 8° in an ice-bath. Camphane (0.93 g., 0.0067 mole) was added and the temperature of the mixture maintained at 10–12°. After five hours a 5-cc. aliquot was titrated, showing that 0.0022 mole of dichromate had been consumed. The reaction was stopped by diluting with ice-water to 500 cc., and the mixture was extracted five times with 50-cc. portions of dichloromethane. The combined extracts were washed with water, dilute sodium carbonate, and water, and finally with one 100-cc. and two 50-cc. portions of concentrated sulfuric acid. The yellow acid extracts were poured into 500 cc. of ice and water. The turbidity of the dilute acid solution was removed by washing with two 15-cc. portions of dichloromethane. This solvent was evaporated to leave 0.5 g. of soft brown crystals, which were sublimed at reduced pressure. The sublimate, which weighed 210 mg., melted at 155–160°, recrystallized m.p. 175–177°.[13] *Anal.* Calcd. for $C_{10}H_{16}O$: C, 78.88; H, 10.60. Found: C, 78.48; H, 10.53.

A 10-mg. sample of the product was introduced into 2 ml. of the usual oxidation mixture. After four hours at room temperature no perceptible darkening had taken place. The product gave a 2,4-dinitrophenylhydrazone, m.p. 173–174°, mixed m.p. with *dl*-camphor 2,4-dinitrophenylhydrazone[14] 140–145°. *Anal.* Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.83; H, 6.02. Found: C, 57.62; H, 6.15. A semicarbazone of this product decomposed at 200° with KOH yielded a hydrocarbon, m.p. 153–155°, which gave no depression in melting point with an authentic sample of *dl*-camphane.

Acknowledgment.—We wish to express our gratitude for the generous support given this work by the Office of Naval Research. We are also indebted to Dr. Bernhard Witkop of the National Institutes of Health for the infrared data.

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(12) This fraction was converted quantitatively into the 2,4-dinitrophenylhydrazone of diethyl ketone, m.p. and mixed m.p. 156°.

(13) Epicamphor m.p. 182°, Y. Asahina and M. Ishidate, *Ber.*, **67B**, 71 (1934).

(14) R. Shriner and R. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., third edition, 1948, p. 265.

WASHINGTON, D. C.

[CONTRIBUTION FROM SOCONY MOBIL LABORATORIES, A DIVISION OF SOCONY MOBIL OIL COMPANY, INC., RESEARCH AND DEVELOPMENT DEPARTMENT]

The Abstraction of Hydrogen Atoms from Liquid Hydrocarbons by *t*-Butoxy Radicals

BY A. L. WILLIAMS, E. A. OBERRIGHT AND J. W. BROOKS

RECEIVED AUGUST 4, 1955

Removal of hydrogen atoms from liquid hydrocarbons by *t*-butoxy radicals has been investigated. The reactivities of hydrogen atoms have been measured by the rate of formation of *t*-butyl alcohol relative to the rate of decomposition of *t*-butoxy radicals to acetone. Ratios of the specific rate constants for the hydrogen abstraction reaction to the specific rate constant for *t*-butoxy radical decomposition have been calculated from the molar ratios of *t*-butyl alcohol to acetone obtained experimentally. The specific rate constant ratios permit a comparison of the reactivities of different types of hydrogen atoms for the abstraction process.

The rates at which hydrogen atoms of various types are removed from gaseous hydrocarbons by methyl radicals have been investigated by Trotman-Dickenson and Steacie.[1] Rate constants (relative to the combination of methyl radicals) characteristic of various types of hydrogen atoms in alkanes were calculated by considering the hydrogen atoms as though they were present in separate molecules in a multicomponent mixture. Application of this treatment to liquids is complicated by the increased probability of combination of methyl radicals to yield ethane.[2]

t-Butoxy radicals permit measurement of the rate of abstraction of hydrogen atoms from liquid hydrocarbons. The rate measurements are rela-

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(1) A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951).

(2) A. F. Trotman-Dickenson, *Quart. Rev.*, **7**, 198 (1953).