TABLE VII

EFFECT OF WATER ON THE pH OF MIXTURES OF SODIUM PERCHLORATE AND PERCHLORIC ACID

$(C_{HClO_4})_t$, M	$(C_{NaClO_4})_t$, M	$(C_{H_2O})_t$, M	$p\mathrm{H}_{exp}$	$p\mathrm{H}_{calcd}$
0.0462	0.104	0.0948	3.84	3.83
.0462	.104	.164	4.04	4.07
.0462	.104	.234	4.25	4.23
.0462	.104	.373	4.51	4.45
.0462	.104	.527	4.63	4.60
.0989	.0889	.0560	3.31	3.29
.0989	.0889	.0815	3.42	3.42
.0989	.0889	.109	3.53	3.53
.0989	.0889	.138	3.63	3.66
.0989	.0889	.165	3.73	3.76

TABLE VIII

EFFECT OF WATER ON THE COLOR OF PNB IN 0.104 M SODIUM PERCHLORATE

$C_{PNB} = 2.96 \times 10^{-5}$ M

Total water concn.	$[IHClO_4]/[I]_{exp}$	$[IHClO_4]/[I]_{calcd.}$ for $K^{NaClO_4} =$ 2.40×10^8	2.6×10^{8a}
0.0315	1.03	1.10	1.04
.0500	.94	1.02	.93
.0685	.89	.93	.89
.106	.78	.82	.78
.180	.67	.69	.66
.328	.54	.54	.52

[a] The value of $K_f^{NaClO_4}$ as calculated from our earlier data is 2.40×10^8. However, as the last column shows using a value of 2.6×10^8 gives much better agreement with experiment. The uncertainty in the formation constant of sodium perchlorate is large enough to justify the use of the higher value.

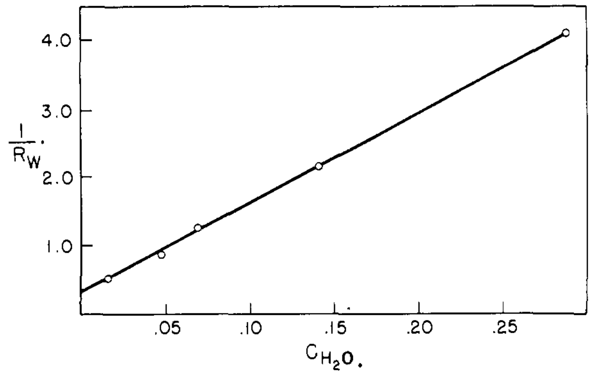

Fig. 2.—Effect of water on R of α-naphtholphthalein in a mixture 0.029 M in perchloric acid and 0.10 M in sodium perchlorate; slope = 13.2; intercept = 0.33.

acetic acid solution containing 2.96×10^{-5} M PNB and 0.104 M $NaClO_4$ is given in Table VIII. Using equation 8c, we have found excellent agreement between calculated and experimental data.

Effect of Water on $[I_a]/[I_b]$ in a Solution of $BHClO_4$ and $HClO_4$.—Using α-naphtholphthalein as the indicator, the effect of water on an acetic acid solution 0.029 M in perchloric acid and 0.10 M in sodium perchlorate was determined. It follows directly from equation 8c that a plot of $1/R_w$ *versus* C_{H_2O} should be a straight line of slope $K_f^{H_3OClO_4}/R_0$ and intercept $1/R_0$. Such a plot is given by Fig. 2 and yields a value of $K_f^{H_3OClO_4}$ equal to 39, in satisfactory agreement with our earlier value of 34.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

The Disproportionation and Combination Reactions of Butyl Free Radicals[1]

BY JOHN W. KRAUS AND JACK G. CALVERT

RECEIVED JUNE 28, 1957

The vapor phase photolyses of di-*t*-butyl, di-iso-butyl, and di-*sec*-butyl ketones are made in full mercury arc light. The rates of formation of the products are determined in experiments at several temperatures, light intensities and ketone concentrations. Product analyses are made by mass spectrometry and vapor partition chromatography. The data suggest the importance of the primary processes: $[(CH_3)_3C]_2CO + h\nu \rightarrow (CH_3)_3C + COC(CH_3)_3$; $[(CH_3)_2CHCH_2]_2CO + h\nu \rightarrow (CH_3)_2CHCH_2 + (CH_3)_2CHCH_2CO$, $[(CH_3)_2CHCH_2]_2CO + h\nu \rightarrow C_3H_6 + CH_3COCH_2CH(CH_3)_2$; $[C_2H_5CH(CH_3)]_2CO + h\nu \rightarrow C_2H_5CHCH_3 + C_2H_5CH(CH_3)CO$, $[C_2H_5CH(CH_3)]_2CO + h\nu \rightarrow C_2H_4 + C_2H_5COCH(CH_3)C_2H_5$. The ratios of the rate constants for the disproportionation reaction, $2C_4H_9 \rightarrow C_4H_8 + C_4H_{10}$ (1), and the combination reaction, $2C_4H_9 \rightarrow C_8H_{18}$ (2), are derived for the different butyl radicals. At temperatures near 100° the ratios of k_1/k_2 are: t-C_4H_9, 4.59; iso-C_4H_9, 0.418; *sec*-C_4H_9, 2.27. If the values for k_2 for the different butyl radicals are near equal then the dominant factor which determines the rate constants for (1) is the number of abstractable hydrogen atoms which can be removed from the radical to form a stable olefin product. Presumably this number is directly related to the probability of formation of the transition state involved in reaction 1, C_4H_8–H–C_4H_9.

Several studies have been made of the disproportionation reaction 1 and the combination reaction 2

$$2R \longrightarrow RH + (R\text{–}H), \text{olefin} \qquad (1)$$

$$2R \longrightarrow R\text{–}R \qquad (2)$$

for the ethyl, n-propyl and isopropyl free radicals. A correlation has been noted between the structure of the radical and the relative rates of the reactions 1 and 2.[2-11] Averages of the best published estimates of k_1/k_2 at 25° for the various radicals are:

---

(1) Presented in part before the Division of Physical and Inorganic Chemistry, 131st Meeting of the American Chemical Society, Miami, Florida, April, 1957. Taken from the thesis of J. W. Kraus submitted in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University, 1957.

(2) F. E. Blacet and J. G. Calvert, THIS JOURNAL, **73**, 661 (1951).

(3) M. H. J. Wijnen and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1092 (1951).

(4) (a) C. R. Masson, THIS JOURNAL, **74**, 4731 (1952); (b) S. G. Whiteway and C. R. Masson, *ibid.*, **77**, 1508 (1955); (c) *J. Chem. Phys.*, **25**, 233 (1956).

(5) R. W. Durham and E. W. R. Steacie, *Can. J. Chem.*, **31**, 377 (1953).

(6) H. T. J. Chilton and B. G. Gowenlock, *Trans. Faraday Soc.*, **49**, 1451 (1953).

(7) (a) P. Ausloos and E. W. R. Steacie, *Bull. soc. chim. Belg.*, **63**, 87 (1954); (b) *Can. J. Chem.*, **33**, 1062 (1955).

(8) R. K. Brinton and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1840 (1955).

(9) C. A. Heller and A. S. Gordon, *J. Phys. Chem.*, **60**, 1315 (1956).

(10) J. T. Gruver and J. G. Calvert, THIS JOURNAL, **78**, 5208 (1956).

(11) A. Shepp and K. O. Kutschke, *J. Chem. Phys.*, **26**, 1020 (1957).

C_2H_5, 0.12; n-C_3H_7, 0.13; iso-C_3H_7, 0.52; *sec*-C_4H_9, 0.61. The previous studies show that $E_1 - E_2 \cong 0$. It is seen that the ratio of k_1/k_2 increases as the branching of the radical increases. It has been suggested that the origin of this effect lies in the greater steric hindrance of the more complex radical and its larger number of hydrogen atoms which can be abstracted to lead to olefin product.[2,7b] The butyl radicals involve a great range of structural types and should provide an excellent test for structure and reactivity correlations. For example, there are nine hydrogen atoms per *t*-butyl radical which can be abstracted in reaction 1 to lead to the product isobutene, while there is but one such hydrogen atom per isobutyl radical.

Experimental

Apparatus.—In the present work the different butyl radicals were produced in vapor phase photolyses of the structurally related dibutyl ketones. Light from the full mercury arc was used as the radiation source to ensure the maximum intensity of absorbed light and high radical concentrations which favor the homogeneous bimolecular reaction modes 1 and 2. The all-glass photolysis system was enclosed in an air thermostat regulated to 100 ± 1° in order to maintain a reasonable concentration of ketone vapor and to avoid condensation of the relatively low vapor pressure liquid ketones. The photolysis system consisted of a cylindrical quartz photolysis cell (420-cc. volume), a Bodenstein manometer, a glass in line circulating pump and a trap. This system was isolated by modified Veeco metal valves enclosed within the thermostat; possible errors due to adsorption or condensation of the reactants and products on stopcock grease was thus eliminated. The photolysis cell was suspended in an aluminum block oven regulated to ±1° and entire assembly placed in the air thermostat. The unfiltered light which completely filled the reaction chamber in all experiments was a collimated beam from an Hanovia Type A (S-500) burner operated on a regulated a.c. power supply. Neutral density filters were used in some cases to reduce the incident light intensity transmitted to the cell.

All products condensed at liquid nitrogen temperature were analyzed by vapor partition chromatography. The chromatography columns were constructed of 5 mm. i.d. Pyrex glass tubing formed into U-shaped tubes, 1 m. in length. The column packing consisted of a solid phase, either activated silica gel or C-22 firebrick (Johns-Manville), with a liquid phase of Dow-Therm A. The column was suspended in a glass tube wrapped with flexible heating tape and the entire tube covered with a Magnesite jacket. The heater voltage was controlled by a Variac and the temperature recorded by a thermocouple. The detector was a Gow-Mac thermoconductivity cell Model NRL, and the electrical circuit was constructed according to the specifications supplied with the cell.

Materials.—$(C_2H_5)_2CO$ and (iso-$C_4H_9)_2CO$ were products of Eastman. The (t-$C_4H_9)_2CO$ and (sec-$C_4H_9)_2CO$ were obtained from Edcan. The ketones were purified by column fractionation at atmospheric pressure and bulb-to-bulb distillation in a high vacuum system. 2-Methylbutanal was prepared and purified by Mr. J. T. Gruver of the Department of Chemistry, The Ohio State University. Reference samples of the C_1 to C_4 hydrocarbons were Phillips Research grade. Pure samples of 2,2,3,3-tetramethylbutane, 2,5-dimethylhexane and 3,4-dimethylhexane were furnished by Dr. K. W. Greenlee of the American Petroleum Institute, The Ohio State University. Standard CO was obtained from Matheson.

Product Analysis.—Less than 3% of the original ketone was decomposed during the photolyses. After photolysis the products were removed from the system in two fractions. The first fraction consisted of products not condensable at liquid nitrogen temperature, CO and CH_4. This fraction was pumped from the photolysis system by a Toepler pump, stored over mercury, the volume measured with a Blacet-Leighton gas buret, and an aliquot sample analyzed by mass spectrometry. The products and excess ketone condensed at liquid nitrogen temperature were distilled from the photolysis system to the trap of the chromatography system and subsequently analyzed. The C_2, C_3 and C_4 hydrocarbons were eluted from the column operated at room temperature. The column temperature was raised to 80° after the last of the C_4 peaks was observed; thus a reasonable elution time for the octanes was obtained without loss of resolution of the lower hydrocarbons. The excess ketone was eluted after the octanes.

Products.—The different products of the photolyses and the rates of their formation are summarized in Tables I and II. The numbers shown in parentheses under the rate values are the approximate average quantum yields of each product. Since a full mercury arc was used for the photolyses, only an approximate over-all product quantum efficiency could be calculated. Our calculation is based on the assumption that $\Phi_{CO} = 1.0$ for di-t-butyl ketone photolyses at temperatures above 100°. This appears to be reasonable in view of the results of Whiteway and Masson from di-isopropyl ketone photolyses.[4b] The ultraviolet absorption spectra of the ketones in the vapor state were determined on a Cary recording spectrophotometer at 20° and a measured pressure in a 10-cm. quartz cell. The extinction coefficients of the ketones were calculated at each wave length in the mercury arc spectrum. The estimated quantum efficiencies were obtained from the calculated fraction of light absorbed at each of the wave lengths, the known energy distribution of the arc, and the rate data for di-t-butyl ketone (average Φ_{CO} assumed = 1.0) and the other ketones.

Preliminary Studies of Diethyl Ketone Photolysis.—In order to test the analytical and photochemical procedures employed in this work two photolyses of diethyl ketone were made at a pressure of 56 mm. and at temperatures of 108 and 110°, respectively. The ratios of the rate of formation of ethylene to that of butane (presumably a measure of k_1/k_2) were estimated as 0.12_8 and 0.14_3. An average of the values reported by Brinton and Steacie[8] is 0.12. The calculated values of the rate function $(R_{C_2H_6} - R_{C_2H_4})/R^{1/2}{}_{C_4H_{10}}[(C_2H_5)_2CO]$ were 0.71_9 and 0.72_5 (cc./mole-sec.)$^{1/2}$, in good agreement with the previous estimates for this temperature. The over-all consistency of these check runs with the previous work in which other analytical means were used seemed reasonable proof that the apparatus and techniques were operating satisfactorily.

Discussion

The Primary Processes in the Photolysis of the Di-butyl Ketones.—The photolysis results can be described well with reference to the following general primary processes

$$(C_4H_9)_2CO + h\nu \longrightarrow C_4H_9CO + C_4H_9\ (2C_4H_9 + CO) \quad \text{(I)}$$

$$\longrightarrow C_nH_{2n} + RCOC_4H_9 \quad \text{(II)}$$

$$\longrightarrow CH_3 + C_3H_6COC_4H_9 \quad \text{(III)}$$

(a) **Primary Process (I).**—There is abundant evidence that primary process I, butyl radical formation, is important with each of the ketones. It will be shown that the octane, butane and butene rate data suggest that these products are formed from butyl free radicals.

In the case of the di-t-butyl ketone photolysis the process I occurs exclusively. The temperature independence of the various product quantum yields and the results of the nitric oxide inhibition runs substantiate this conclusion. In the runs in the presence of nitric oxide (11, 12 of Table I) the normal products, isobutane and 2,2,3,3-tetramethylbutane, are absent, and it can be seen that $R_{\text{iso-}C_4H_8}$ is approximately twice as great as the rate of this product in the runs 1 and 10 made under similar experimental conditions but in the absence of NO. This is consistent with the occurrence of process I followed by reactions 3-6 in the runs with added nitric oxide.

$$(CH_3)_3C + NO \longrightarrow (CH_3)_3CNO \quad (3)$$

$$(CH_3)_3CNO \longrightarrow \text{iso-}C_4H_8 + HNO \quad (4)$$

TABLE I

RATES OF FORMATION OF PRODUCTS AND ESTIMATED QUANTUM EFFICIENCIES FROM DI-*t*-BUTYL KETONE PHOTOLYSIS WITH FULL MERCURY ARC

Run	Time, sec.	Press., mm.	I_0, relative	Temp., °C.	$[R_2CO]$, moles/cc. × 10^6	Product rates, moles/cc.-sec. × 10^{12}; estimated av. quantum efficiencies in parentheses CO	Iso-C_4H_{10}	Iso-C_4H_8	2,2,3,3-Tetramethylbutane	k_2/k_1
1	600	22.0	100	117.0	0.905	22.5 (1.14)	12.2 (0.62)	14.0 (0.71)	2.57 (0.13)	0.20
2	600	23.5	56	114.9	.971	12.2 (1.08)	7.89 (0.70)	8.92 (0.79)	1.96 (0.17)	.23
3	1320	23.5	39	117.6	.963	8.04 (1.02)	5.44 (0.69)	5.74 (0.73)	1.23 (0.15)	.22
4	600	10.0	100	118.1	.410	10.5 (0.88)	6.86 (0.58)	8.23 (0.69)	1.70 (0.14)	.23
5	660	40.5	100	119.0	1.65	25.2 (0.99)	16.9 (0.67)	19.3 (0.76)	3.36 (0.13)	.19
6	900	26.3	100	178.0	0.935	19.8 (1.06)	13.0 (0.70)	15.0 (0.80)	3.16 (0.17)	.26
7	900	28.9	100	250.7	.884	16.3 (0.84)	12.0 (0.61)	13.7 (0.70)	3.30 (0.17)	.23
8	1200	33.3	0	322.2	.897	1.58	0.49	4.04	0.09	..
9[a]	1292	33.2	100	321.8	.895	16.0 (0.82)	11.0 (0.56)	10.8 (0.55)	2.0 (0.10)	.18
10	1300	23.2	100	102.0	.985	23.6 (1.15)	14.0 (0.67)	15.3 (0.74)	3.50 (0.17)	.24
11[b]	600	23.2	100	104.8	.983	....	0.0	27.1 (1.31)	0.0	..
12[c]	600	23.8	100	106.9	1.00	....	0.0	22.1 (1.08)	0.0	..

[a] Rates corrected for thermal decomposition as measured in run 8; results can be considered to be only approximate. [b] Run with added nitric oxide at 29.3 mm. [c] Run with added nitric oxide at 10.5 mm.

TABLE II

RATES OF FORMATION OF PRODUCTS AND ESTIMATED QUANTUM EFFICIENCIES FROM THE PHOTOLYSIS OF DI-ISO-BUTYL AND DI-*sec*-BUTYL KETONES AND 1-METHYLBUTANAL IN FULL MERCURY ARC LIGHT

Run	Time, sec.	Press., mm.	I_0, relative	Temp., °C.	$[R_2CO]$, moles/cc. × 10^6	Product rates, moles/cc.-sec. × 10^{12}; estimated av. quantum efficiencies in parentheses CO	Iso-C_4H_{10}	Iso-C_4H_8	C_3H_6	CH_4	2,5-Dimethylhexane	$\frac{R_{C_8H_{18}}}{R_{C_4H_8}}$	$k_1/k_2{}^{1/2}$
						(a) Di-iso-butyl ketone							
1	4500	21.9	100	78.0	1.00	2.92 (0.18)	0.47 (0.028)	0.198 (.012)	6.30 (0.38)	0.024 (.001)	0.479 (.029)	2.42	0.39
2	4500	40.6	100	102.0	1.74	3.94 (0.17)	2.12 (0.092)	.304 (.013)	8.52 (0.37)	.065 (.003)	.0812 (.035)	2.67	1.14
3	3570	23.8	100	108.2	1.00	3.20 (0.19)	0.961 (.058)	.170 (.010)	5.32 (0.32)	.074 (.004)	.417 (.025)	2.45	1.22
4	9000	23.8	39	108.9	1.00	1.10 (0.17)	.589 (.093)	.080 (.013)	2.33 (0.37)	.021 (.003)	.163 (.026)	2.03	1.29
5	4500	26.9	100	155.9	1.00	3.57 (0.21)	2.34 (0.141)	8.52 (0.514)	5.94 (0.36)	.070 (.004)	.426 (.026)	0.48	3.34
6	4500	29.8	100	193.9	1.02	5.59 (0.33)	5.16 (0.306)	3.40 (0.202)	7.14 (0.43)	.051 (.003)	.519 (.031)	0.15	6.73
						(b) Di-*sec*-butyl ketone							
						n-C_4H_{10}	1-C_4H_8	*cis*-2-C_4H_8	*trans*-2-C_4H_8	C_2H_4	3,4-Dimethyl hexane		$\frac{R_{C_8H_{18}}}{R_{C_4H_8}}$
1	4500	21.8	100	98.1	0.940	2.57 (0.19)	1.24 (0.091)	0.200 (.015)	0.597 (.044)	3.74 (0.273)	0.911 (.067)		0.45
2	7200	23.3	39	105.1	.987	1.25 (0.23)	.615 (.112)	.106 (.019)	.313 (.057)	1.77 (0.322)	.413 (.075)		.40
3	4500	37.4	100	101.3	1.60	3.55 (0.19)	1.72 (0.093)	.614 (.033)	1.16 (0.063)	5.12 (0.278)	1.62 (0.088)		.46
						(c) 2-Methylbutanal							
1	1800	49.4	100	102.0	2.11	12.4	0.655	0.230	0.431	...	0.552		.42

or

$$(CH_3)_3C + NO \longrightarrow \text{iso-}C_4H_8 + HNO \qquad (5)$$

$$HNO \longrightarrow \text{Products not identified} \qquad (6)$$

The possible product $(CH_3)_3CNO$ was not detected in the chromatographic analysis although the characteristic blue color of this liquid was observed in the liquid fraction of the products.[12] It appears that the greatest share of the molecules of this compound, if it is formed at all, decompose homogeneously or on the chromatographic column packing according to reaction 4. It will be shown in the discussion which follows that the ratio $k_1/k_2 = 4.5_9$ and hydrogen abstraction is unimportant for the *t*-butyl radical. If this is the case then the above mechanism is consistent with the experimental results; according to the proposed mechanism most of the *t*-butyl radicals form iso-C_4H_8 in the nitric oxide inhibited runs and only about half of them form this product in the dominant disproportionation reaction 1 of the uninhibited runs.

At the temperatures usually employed in this study ($t > 100°$), it is likely that the C_4H_9CO radi-

---

(12) E. Bamberger and R. Seligman, *Ber.*, **36**, 685 (1903).

cal decomposes into C_4H_9 and CO almost exclusively following its formation in (I). Then for our purposes we may consider that two butyl radicals and a carbon monoxide molecule are the products of primary process I. Hence the rate of CO formation is a measure of the rate of process I, providing that there is no formation of CO in other reactions. From the non-chain carbon monoxide rates the following approximate over-all quantum efficiencies of the primary process I for the butyl ketones are estimated: di-*t*-butyl ketone, 1.0 (assumed); di-iso-butyl ketone, 0.19; di-*sec*-butyl ketone, 0.37.

(b) **Primary Process (II).**—Process II, the intramolecular formation of olefin and smaller ketone, is important for the di-iso-butyl and di-*sec*-butyl ketones; presumably C_3H_6 and $CH_3COCH_2CH(CH_3)_2$ form from the iso-butyl ketone and C_2H_4 and $C_2H_5COCH(CH_3)C_2H_5$ from the di-*sec*-butyl ketone. The relative temperature, light intensity and pressure independence of the quantum yields of the products C_3H_6 and C_2H_4 suggest this mode of formation. Quantitative analysis for the ketone products was not accomplished, but there were chromatographic peaks observed from the liquid products with elusion times consistent with those expected for these compounds. Process II is completely analogous to the Norrish "Type II" primary processes suggested for methyl *n*-butyl ketone,[13] methyl *n*-propyl ketone,[14] *n*-butyraldehyde,[15] di-*n*-propyl ketone,[4a,b] methyl neopentyl ketone,[16] methyl *n*-amyl ketone,[14b] and 2-methylbutanal.[10] The ketones and aldehydes which have an alkyl side chain of at least three carbon atoms in length attached to the carbonyl group undergo an intramolecular primary process analogous to II without known exception. In this process the product molecules of the olefin and the ketone or aldehyde form by the rupture of the bond between the α- and β-carbon atoms with the simultaneous transfer of a γ-hydrogen atom to the product carbonyl molecule. Differentiation between the alternative γ-hydrogen transfer mechanisms suggested by Davis and Noyes[13c] is not possible from present data. As a qualitative rule the greater the number of γ-hydrogen atoms in the compound the greater is the efficiency of the process. Thus process II is more important for di-iso-butyl ketone ($\phi_{II} = 0.37$) with its twelve γ-hydrogens than for di-*sec*-butyl ketone ($\phi_{II} = 0.29$) with its six γ-hydrogens.

An additional primary process III of minor importance ($\phi_{III} = 0.003$) is proposed to explain the independence of the quantum yields of methane to the experimental variables in di-isobutyl ketone photolysis. It appears that similar reactions forming CH_3 and C_2H_5 radicals occur in the di-*sec*-butyl ketone photolyses, but in this case quantitative rate data were not obtained on the non-condensable fraction of the products, and the efficiencies cannot be estimated.

The Disproportionation, Combination and Hydrogen-abstraction Reactions of the Butyl Radicals.—The present data provide some interesting information about the butyl radical reactions 1, 2 and 7.

$$2C_4H_9 \longrightarrow C_4H_8 + C_4H_{10} \qquad (1)$$

$$2C_4H_9 \longrightarrow C_8H_{18} \qquad (2)$$

$$C_4H_9 + (C_4H_9)_2CO \longrightarrow C_4H_{10} + C_4H_8COC_4H_9 \qquad (7)$$

(a) **The *t*-Butyl Free Radical.**—Several significant results from the di-*t*-butyl ketone photolysis should be noted from the data of Table I. It can be seen that $\Phi_{C_4H_8} \cong \Phi_{C_4H_{10}}$, and $\Phi_{CO} \cong \Phi_{C_8H_{18}} + (\Phi_{C_4H_8} + \Phi_{C_4H_{10}})/2$. There is no consistent trend in either of these functions or the quantum yields of any of the products with change in light intensity, ketone concentration, and temperature. The minor but consistent divergence of both functions from equality probably arises from a solubility difference of the products in the large ketone excess. The effect of nitric oxide described in the preceding section proves that free radicals are involved as intermediates to the final products formed. All of these results can be explained best assuming that (1) and (2) are the major reactions which follow the only primary process, I. With this interpretation the rate ratio $2R_{C_8H_{18}}/(R_{C_4H_8} + R_{C_4H_{10}})$ was used to obtain best estimates of k_2/k_1 shown in the last column of Table I. The constancy of this ratio with variation in light intensity and concentration of ketone is in accord with the mechanism presented. The average of these estimates gives $k_2/k_1 = 0.22$. The insensitivity of the ratio to temperature variation suggests $E_1 \cong E_2$. The present estimate agrees well with $k_2/k_1 = 0.22$ at 25° derived by Trotman-Dickenson[17] from the $R_{C_8H_{18}}/R_{C_4H_{10}}$ ratio from the mercury photosensitized hydrogenation of isobutene.[18] It is considerably different from the value of 0.15 estimated from the same study at 300°. In the 300° run of Moore and Wall it is likely that a significant fraction of the butane is formed from butyl radicals by hydrogen-abstraction from the isobutene excess, and the measured ratio $R_{C_8H_{18}}/R_{C_4H_{10}}$ must be less than the actual value of k_2/k_1 in this case.

The unimportance of the hydrogen-abstraction reaction 7 in the present system up to 320° is somewhat surprising. It suggests that the activation energy E_7 for the *t*-butyl radical reaction 7 is unusually large; the relatively high energy of the activated complex in this case may reflect the strength of the primary C–H bond in the parent ketone and the weakness of the tertiary C–H bond in the product isobutane. In view of the unimportance of 7 under the present experimental conditions the di-*t*-butyl ketone is an attractive source of *t*-butyl radicals for the study of the hydrogen-abstraction reactions of *t*-butyl with added compounds.

(b) **The Isobutyl Free Radical.**—The quantum yield of isobutene and the ratio of $R_{C_8H_{18}}/R_{C_4H_8}$ is insensitive to temperature, light intensity and pres-

---

(13) (a) R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 874 (1934); (b) C. H. Bamford and R. G. W. Norrish, *ibid.*, 1531, 1544 (1938); (c) W. Davis, Jr., and W. A. Noyes, Jr., THIS JOURNAL, **69**, 2153 (1947).

(14) (a) A. J. C. Nicholson, *Revs. Pure Applied Chem.*, **2**, 174 (1952); (b) *Trans. Faraday Soc.*, **50**, 1067 (1954).

(15) (a) P. A. Leighton, L. D. Levanas, F. E. Blacet and R. D. Rowe, THIS JOURNAL, **59**, 1843 (1937); (b) F. E. Blacet and J. G. Calvert, *ibid.*, **73**, 667 (1951).

(16) T. W. Martin and J. N. Pitts, Jr., *ibid.*, **77**, 5465 (1955).

(17) A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press, Inc., New York, N. Y., 1955, p. 236.

(18) W. J. Moore and L. A. Wall, *J. Chem. Phys.*, **17**, 1325 (1949).

sure of ketone up to 109° (see Table II), and it is likely that C_4H_8 and C_8H_{18} are formed only in reactions 1 and 2 under these conditions. The average ratio from the low temperature runs gives $k_2/k_1 = 2.3_9$ (78–109°).

At temperatures $\geq 150°$ the ratios of $R_{C_8H_{18}}/R_{C_4H_8}$ decrease rapidly with temperature rise, and the rates of formation of CO, C_4H_{10} and C_4H_8 show evidence of the onset of a chain reaction. These chain reactions are suggested

$$(CH_3)_2CHCH_2 + [(CH_3)_2CHCH_2]_2CO \longrightarrow \text{iso-}C_4H_{10} + (CH_3)_2CCH_2COC_4H_9 \quad (7')$$

$$(CH_3)_2CCH_2COC_4H_9 \longrightarrow \text{iso-}C_4H_8 + COC_4H_9 \quad (8)$$

$$COC_4H_9 \longrightarrow CO + (CH_3)_2CHCH_2 \quad (9)$$

Assuming reactions 1, 2, 7′, 8, and 9 follow primary process I we may obtain information concerning the hydrogen-abstraction reaction 7′ from the function 10.

$$(R_{C_4H_{10}} - R_{C_4H_{10}(1)})/R^{1/2}{}_{C_8H_{18}}[R_2CO] = k_7'/k_2^{1/2} \quad (10)$$

$R_{C_4H_{10}(1)}$ is the rate of butane formation in reaction 1; this was estimated from the measured octane rates assuming $k_2/k_1 = 2.3_9$ independent of temperature. An Arrhenius plot of the calculated values of $k_7'/k_2^{1/2}$ is given in Fig. 1. The least squares treatment of the data give: $k_7'/k_2^{1/2} = 2.6_4 \times 10^4e^{-7.6/RT}$ (cc./mole-sec.)$^{1/2}$. It is interesting to compare this result with that of Trotman-Dickenson, *et al.*,[19] obtained for an analogous reaction involving CH_3 radicals.

$$CH_3 + (CH_3)_3CH \longrightarrow CH_4 + C(CH_3)_3 \quad (11)$$

$$2CH_3 \longrightarrow C_2H_6 \quad (12)$$

Their data yield $k_{11}/k_{12}^{1/2} = 1.5 \times 10^4e^{-7.6/I.T}$ (cc./mole-sec.)$^{1/2}$. The similarity of these two rate functions is striking. Since both reactions 7′ and 11 involve the formation of a primary C–H bond and the rupture of a tertiary C–H bond, and since it is likely that $k_2 \cong k_{12}$, the result can be rationalized.

(c) **The *sec*-Butyl Free Radical.**—In this case the disproportionation reaction 1 may lead to three different butene products depending on which of the hydrogen atoms of the radical is abstracted.

$$2CH_3CH_2CHCH_3 \longrightarrow 1\text{-}C_4H_8 + n\text{-}C_4H_{10} \quad (1')$$

$$\longrightarrow cis\text{-}2\text{-}C_4H_8 + n\text{-}C_4H_{10} \quad (1'')$$

$$\longrightarrow trans\text{-}2\text{-}C_4H_8 + n\text{-}C_4H_{10} \quad (1''')$$

The rate data are summarized in Table II. The complexity of the products of the di-*sec*-butyl ketone photolyses was much greater than that of the other ketones. Qualitative evidence was found for methyl and ethyl radical formation, presumably in primary processes analogous to III. This could have led to complications through butene formation by methyl and ethyl radical interaction with butyl radicals. The limited data show $R_{C_8H_{18}}/R_{C_4H_8}$ to be insensitive to the light intensity and ketone pressure variation. If we assume no complications then we estimate from these data that $k_2/(k_1' + k_1'' + k_1''') = 0.44$ near 100°. The uncertainty in the interpretation in this case prompted the use of 2-methylbutanal photolysis as an independent source of *sec*-butyl radicals. The photolysis of this compound shows a very minor contribution from a methyl radical forming primary process and ethyl radical formation is negligible.[10] The data for this run are shown in Table II. The derived ratio, $k_2/(k_1' + k_1'' + k_1''') = 0.42$, is a reasonable check on the values found from the di-*sec*-butyl ketone photolysis and substantiates the interpretation of the ketone results.[20]

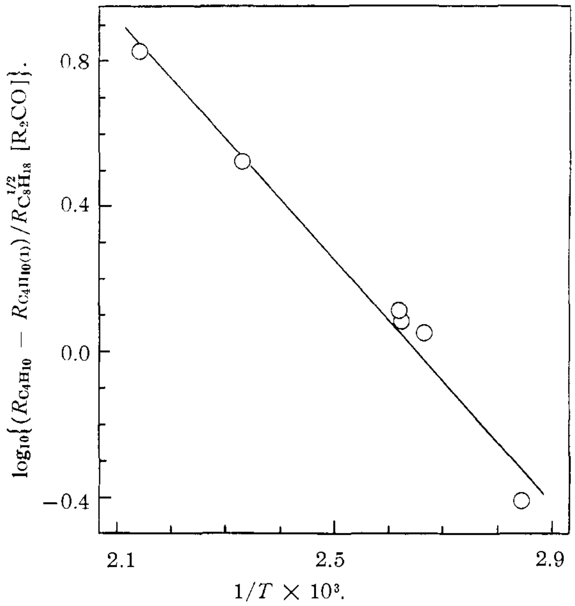

Fig. 1.—Arrhenius plot of the rate function theoretically equal to $k_7'/k_2^{1/2}$. The least squares treatment of the data gives: $k_7'/k_2^{1/2} = 2.64 \times 10^4e^{-7.6/RT}$ (cc./mole-sec.)$^{1/2}$.

Within the experimental error the ratio of the *cis*- to *trans*-2-butene (average of about 0.4) is near the thermodynamic equilibrium value for this temperature.

Correlations between the Butyl Radical Structure and the Relative Rates of the Disproportionation and Combination Reactions.—Summarized in column 1 of Table III are the best estimates of the ratio of k_1/k_2 derived in this work for temperatures near 100°. Ausloos and Steacie[7b] made the interesting observation that the assumption of the equality of the rate constant for the combination reaction involving isopropyl radicals and that for the *n*-propyl radicals leads to a semiquantitative prediction of the rate constants for the disproportionation reactions of these radicals. If one makes the analogous assumption that the rate constants k_2 for the combination reactions of the butyl radicals are equal, then the ratio k_1/k_2 should be proportional to the values of k_1. Column 2 of Table III shows the relative values of rate constants for the disproportionation reaction, ak_1, derived in this fashion and normalized so that ak_1 for the *sec*-butyl radical is equal to 5.0. The number of abstract-

---

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

[20] The butene rate data in this work are based on product analysis by chromatographic techniques and have a much greater accuracy than the less selective mass spectrometric method used in the previous study.[10] The determination of small amounts of butenes in a large amount of butane by mass spectrometry is much less accurate than was realized by Gruver and Calvert. Little weight should be given to the previous estimates of k_2/k_1 for the *sec*-butyl radical. The value of the rate function 11 of ref. 10 calculated using the present data is in good agreement with the previous estimates[10] and indicates the reliability of the analytical data for products other than that for the butenes in the previous work.

able hydrogen atoms per radical which can be removed to lead to an olefin product are listed for comparison in column 3 of Table III.

TABLE III

THE RATE CONSTANTS FOR THE DISPROPORTIONATION (k_1) AND COMBINATION (k_2) REACTIONS FOR THE BUTYL RADICALS NEAR 100°

Radical	(1) k_1/k_2	(2) $ak_1 = 2.2k_1/k_2$ (assuming the k_2's are equal)	(3) No. of H-atoms/radical which lead to olefin when abstracted
t-C_4H_9	4.5_9	10.1	9
Iso-C_4H_9	0.41_8	0.92	1
sec-C_4H_9	2.2_7	5.0	5

There is a striking similarity between the numbers in columns 2 and 3 of Table III. This points up a rather unexpected near quantitative correlation between the structure and rates of reactions 1 and 2. Providing that the assumption of the equality of the k_2 values is justified, it can be concluded that the dominant factor which determines the rate of disproportionation reaction of the butyl radicals is the number of abstractable hydrogens which can be removed from the radical to form a stable olefin product. Presumably this number is directly related to the probability of formation of the transition state involved in reaction 1, C_4H_8–H–C_4H_9.

Further evidence for the near correctness of this simple picture is had in the *sec*-butyl radical results. The average ratio $R_{2\text{-}C_4H_8}/R_{1\text{-}C_4H_8}$ from the results of the two most reliable runs 1 and 2 of Table II (resolution of the butene peaks was best in these runs) is 0.66; the ratio of the number of abstractable H-atoms on the *sec*-butyl radical which can lead to 2-butene to that which can lead to 1-butene is 0.67. Although some qualitative correlation was anticipated, the near quantitative nature of that found was wholly unexpected.

From the present results one is tempted to predict that k_1/k_2 will be equal to about 0.9_2 near 100° for *n*-butyl radicals. There are no reliable data for the *n*-C_4H_9 reactions available now to check this estimate.

The results provide rather indirect evidence for the near equality of the rate constants for the combination reactions of the different butyl radicals. This conclusion is somewhat surprising in the light of the widespread feeling that the combination of *t*-butyl radicals should have an activation energy of a "few" kcal./mole,[21] while that for the other butyl radicals is expected to be near zero. If one attributes the difference between the measured ratio $(k_1/k_2)_{t\text{-}C_4H_9}/(k_1/k_2)_{iso\text{-}C_4H_9} = 11.0$ and the simple theoretical ratio of 9.0 to an activation energy difference for the reaction 2 for *t*-butyl and that for iso-butyl radicals, then he estimates that $(E_2)_{t\text{-}C_4H_9} - (E_2)_{iso\text{-}C_4H_9} = 0.15$ kcal./mole. Assuming a planar configuration for the *t*-butyl radical one intuitively expects that an activation energy somewhat greater than 0.15 kcal./mole for reaction 1 would be necessary to effect the transformation of the planar radicals to the tetrahedral form in the final octane product. However the results presented here do not provide any significant evidence for the hypothesis of the tetrahedral configuration of the alkyl free radicals since the magnitude of the energy for the planar to tetrahedral transformation is a matter of pure speculation with our present limited knowledge of the properties of the *t*-butyl radical.

COLUMBUS, OHIO

---

[21] *E.g.*, see reference 17, p. 307.