rate arise from the mutual compensation of quite large variations of the energy and entropy terms. That entropy and heat of activation tend to compensate each other yielding a minimum of free energy change, is quite a general phenomenon. However, it will be noted in these examples that the direction of the rate change is determined by the entropy rather than the heat change, whereas most commonly it is the other way around. The phenomenon is not exceptional, however, and several examples of such a behavior are reported in literature.[24,25] The present case seems to fit with the observation that for the nucleophilic reactions at the carbon atom the β-substitution in the substrate causes large variations both in the entropy and in the heat change. This has been interpreted as a steric effect,[26] and it may be so also in the present case.

However, the comparison of the allyl and ethyl systems, for which a tenfold variation of the rate is observed, deserves a more thorough discussion. In the allyl compound there is a vinyl group in the β-position whereas, in the ethyl compound, there is a methyl group. As far as inductive electronic effects are concerned the vinyl group is known to be electron attracting while the methyl group is known to be electron releasing. If the structure of the intermediate is IV it may be expected that the introduction of an electron attracting group destabilizes the complex, and *vice versa* if the structure is V. Therefore, neglecting for a moment the steric effect, it could be concluded that structure IV is the more nearly correct. Let us see now how big a contribution of steric effect there might be in this particular example. The substitution of a methyl group by a vinyl one should roughly correspond to the substitution of a methyl by an ethyl group. Taking for comparison the nucleophilic reactions at the carbon atom, the difference in rate, due to steric effect, should correspond to the difference between *n*-propyl and *n*-butyl derivatives. At least for halogen substitution this difference is very small and negligible, although it may become larger when incoming and outgoing groups are as large as the SO_3 groups. Yet it seems hard to attribute the entire decrease in rate to steric effect only, but it appears more reasonable to attribute it to steric plus electronic inductive effects acting in the same direction, and conclude that structure V contributes little to the intermediate, the latter being more correctly represented by the hybrid IV. We think, however, that the study of other systems, for which the steric effect is more clearly separable from the electronic one, is highly advisable. Such systems are for instance the *p*-substituted benzyl thiosulfates (such as p-NO_2 and p-OCH_3) for which the steric effect could be considered constant and the variations in rate could be attributed to electronic effects only.

Acknowledgment.—The authors are indebted to Professors R. E. Powell and R. E. Connick of the University of California at Berkeley for many helpful discussions and suggestions during the preparation of the manuscript.

PADOVA, ITALY

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

The Vapor Phase Photolysis of 2-Methylbutanal at Wave Length 3130 Å.[1]

BY JERRY T. GRUVER AND JACK G. CALVERT

RECEIVED MAY 17, 1956

Vapor phase photolyses of 2-methylbutanal are made in 3130 Å. and full mercury arc light. CO, H_2, CH_4, C_2H_4, C_3H_6, 1- and 2-C_4H_8, n-C_4H_{10} and 3,4-dimethylhexane are the products identified. The quantum yields or rates of the products are determined in experiments at various temperatures, concentrations and intensities. The data suggest the importance of two primary processes: $C_2H_5CH(CH_3)CHO + h\nu \rightarrow C_2H_5CHCH_3 + CHO$ and $C_2H_5CH(CH_3)CHO + h\nu \rightarrow C_2H_4 + C_2H_5CHO$. Activation energies and pre-exponential factors for the decomposition, H-abstraction, disproportionation and combination reactions of the *sec*-butyl radical are derived from the data.

The photolysis of 2-methylbutanal was investigated to determine its value as a source of *sec*-butyl radicals, and to establish the effect of 2-methyl substitution on the efficiency of the ethylene forming primary process of *n*-butyraldehyde photolysis.

Experimental

Apparatus.—The all-glass photolysis system consisted of a quartz photolysis cell (50 mm. long, 30 mm. diam.), a glass circulating pump and a trap. This system was isolated from stopcocks by mercury valves. The cell was suspended in an aluminum block furnace (regulated to ±1°). Radiation from a Hanovia type A (S-500) burner, operated on a regulated 3 amp. a.c. current, was filtered to isolate wave length 3130 Å.[2] The light beam was collimated by a series of lenses and stops so that a fairly homogeneous beam of radiation filled the cell volume (35.3 cc.) almost completely. The geometric arrangement of all components in the light train remained fixed during the study at 3130 Å. The incident intensity was lowered in some runs with uniform density filters. A photomultiplier–amplifier system was used to measure the fractions of light absorbed. Absolute intensities were estimated by acetone vapor photolysis (at temperatures near 110°) at spaced intervals during the course of the photochemical runs. In one series of runs the filter system was removed, the arc moved near to the cell, and a single lens was used for collimation. In these experiments the full radiation of the mercury arc was incident on the cell, and the absorbed intensity ($2500 < \lambda < 3200$ Å.) was estimated by acetone photolysis to be about 90 times the maximum intensity used in the 3130 Å. experiments.

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(1) Presented in part before the Division of Physical and Inorganic Chemistry, 129th Meeting of the American Chemical Society, Dallas, Texas, April, 1956.

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Materials.—2-Methylbutanol ($[\alpha]^{25}D$ $-5.76°$), obtained by fractional distillation of fusel oil, was provided by D. K. Brain and Professor Harold Shechter at The Ohio State University. Optically active 2-methylbutanal was prepared by oxidation of the alcohol with a chromic oxide–pyridine complex. To 250 g. of pyridine at 10–15°, 45 g. (0.48 mole, 15% excess) of chromic oxide was added over a 1-hr. period. A bright yellow slurry resulted. Fifty grams (0.57 mole) of 2-methylbutanol in 200 g. of pyridine was added to this slurry over a period of 2 hr., the temperature held at 15–20°. The mixture turned black on the addition of the alcohol. It was allowed to stand 16 hr. and was then fractionally distilled. The distillate was removed at 65–75° (750 mm.), and it separated into two layers. The lighter aldehyde layer was washed twice with 2 *N* sulfuric acid solution saturated with sodium sulfate and once with a saturated sodium carbonate solution. The aldehyde was then added to a saturated solution of sodium bisulfite and the white adduct which resulted was separated by filtration, washed well with ether and dried. The adduct was then decomposed with a saturated solution of sodium carbonate, the aldehyde layer separated, dried over calcium chloride and distilled, 89.5–91.0° (750 mm.) (uncor.); lit., 90–92° (760 mm.).[3] A middle cut was further fractionated by bulb-to-bulb distillation at reduced pressures and was used as the photolysis sample. The optical activity of the product was unnecessary for this phase of our work but was desired for other photochemical studies.

Reference samples of the gases n-C_4H_{10}, 1- and 2-C_4H_8, C_3H_6, C_2H_4 and CH_4 were Phillips research grade. A sample of 3,4-dimethylhexane was provided by Dr. Kenneth Greenlee of the American Petroleum Institute. Carbon monoxide was prepared by the action of concentrated sulfuric acid on sodium formate, and purified in the conventional manner.[4]

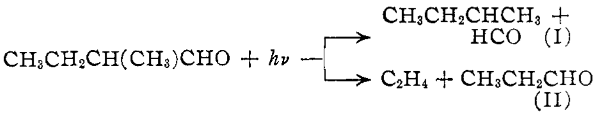
Product Analysis.—After photolysis the products were removed from the system in three fractions. The first fraction, CO, H_2 and CH_4, was removed using a Toepler pump, with the remaining products and excess aldehyde condensed in the trap at N_2(l.) temperature. The second fraction, C_2H_4, C_3H_6, C_4H_8 and C_4H_{10}, was pumped off with the trap at the temperature of Dry Ice–acetone. The third fraction containing unreacted aldehyde and C_8H_{18} was trapped in one arm of a U-tube bulb and allowed to vaporize and contact (for 16 to 24 hr.) potassium hydroxide pellets contained in the other arm. At this time most of the aldehyde had polymerized and analysis for the C_8H_{18} was made mass spectrometrically. CO was analyzed chemically using a Blacet–Leighton gas analysis system,[5] and all other products were determined with a General Electric Analytical mass spectrometer.

Products.—CO, H_2, CH_4, C_2H_4, C_3H_6, C_4H_8 (mixture of 1- and 2-butenes) and n-C_4H_{10} were identified as the major gaseous products. C_8H_{18} (3,4-dimethylhexane) was shown to be present among the condensable products. The quantum yields of these products from photolyses at 3130 Å. and the rate data from runs at full arc are summarized in Tables I and II, respectively. A dashed line in Table I indicates that analysis for this product was not made. The values enclosed in parentheses are considered unreliable because of experimental difficulties encountered in their determination; these were not used in the quantitative treatment of the data. In the relatively long runs required in the 3130 Å. experiments, thermal corrections for the products CO (25%) and CH_4 (3.5%) were necessary at the highest temperature.

Molar Extinction Coefficients.—Molar extinction coefficients were determined for the absorption of 3130 Å. radiation by 2-methylbutanal at various temperatures. The coefficient showed a small increase over the temperature range, from 10.2 (24.5°) to 12.9 (313.0°).

Discussion

Primary Processes.—The results are consistent with the occurrence of the two major primary processes I and II.



$$CH_3CH_2CH(CH_3)CHO + h\nu \begin{cases} \rightarrow CH_3CH_2CHCH_3 + HCO & (I) \\ \rightarrow C_2H_4 + CH_3CH_2CHO & (II) \end{cases}$$

Process I followed by the thermal reactions of *sec*-C_4H_9 and HCO radicals is suggested by the temperature and intensity variations of the quantum yields of the products, CO, C_4H_{10}, C_4H_8, C_8H_{18}, CH_4 and H_2 (see Table I and Figs. 1 and 2). It is likely that H_2 is formed only in the non-chain sequence, I, (5), (6) and (7) (see the discussion of H_2 mechanism which follows). The decomposition reaction, *sec*-

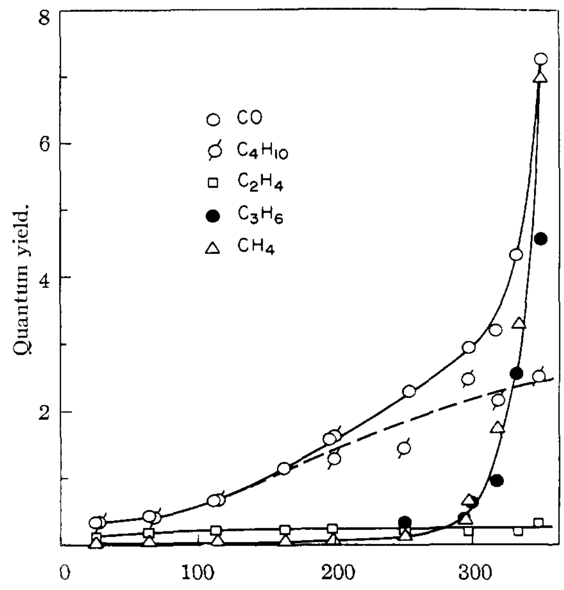


Fig. 1.—The quantum yields of the major products of 2-methylbutanal photolysis at wave length 3130 Å. *vs.* temperature.

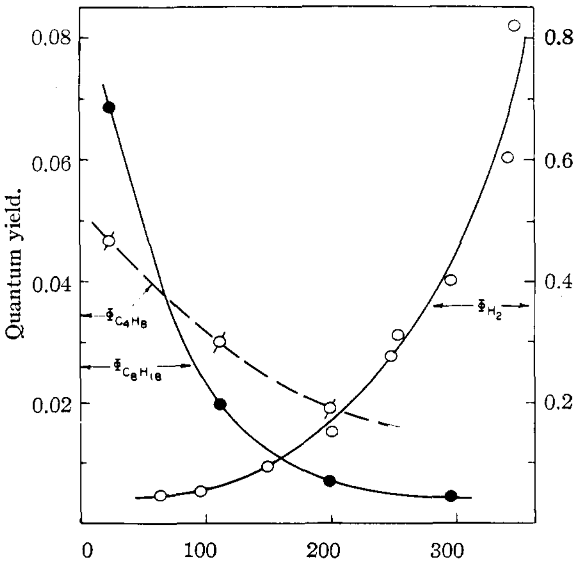


Fig. 2.—The quantum yields of the minor products of 2-methylbutanal photolysis at wave length 3130 Å. *vs.* temperature.

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TABLE I

QUANTUM YIELDS OF PRODUCTS FROM THE PHOTOLYSIS OF 2-METHYLBUTANAL AT 3130 Å.

Run	Temp., °C.	I_a, Ein./l.-sec. × 10^9	[C_4H_9CHO] M × 10^3	Quantum yields CO	H₂	CH_4	C_2H_4	C_3H_6	C_4H_8	C_4H_{10}	C_8H_{18}
1	24.5	9.48	1.44	0.352	...	0.001	0.123	0.00	0.071	0.372	...
2	24.5	7.14	1.55	0.364	...	...	.121	.00	.047	(.244)	0.069
3	64.5	11.22	1.73	0.443	0.046	.024	.167	.00	.045	.399	...
4	97.8	6.86	1.35	...	.053	...	...	..	...	...	...
5	112.0	8.44	1.55	0.605	.047	...	.183	.00	.030	(.388)	0.020
6	112.3	10.45	1.55	0.681	...	.034	.216	.00	.050	.675	...
7	148.8	5.62	1.11	...	.094	...	...	..	...	...	...
8	162.8	10.59	1.51	1.15	.155	.072	.205	.00	.010	.659	...
9	196.1	11.36	1.57	1.59	...	.041	.231	.00	.068	1.64	...
10	200.5	8.91	1.51	1.29	.153	.023	.172	.00	.019	(1.30)	.007
11	201.1	6.22	1.17	...	.213	...	...	..	...	...	...
12	207.9	3.03	1.32	1.81	.157	.073	.200	.00	.039	1.26	(.021)
13	246.4	2.68	1.11	1.87	...	.177	.27	.29	.047	1.61	...
14	248.6	3.51	0.97	1.90	.268	.155	.23	.21	.035	1.21	...
15	248.9	6.44	1.15	...	.277	...	...	..	...	...	...
16	249.5	6.87	1.07	2.42	...	.112	.24	.32	(.056)	1.46	...
17	253.7	10.83	1.39	2.29	.316	.414	.25	.16	...	...	...
18	292.9	9.21	1.40	2.27	(.227)	.366	.19	.41	(.059)	(1.59)	.004
19	295.3	6.83	1.16	...	.403	...	...	..	...	...	...
20	295.9	11.60	1.42	2.93	(.841)	.658	.34	.63	(.073)	2.49	...
21	316.5	8.51	1.25	3.22	(.284)	1.72	(.10)	.96	.0	(1.38)	...
22	331.5	8.55	1.24	4.34	(.189)	3.28	.19	2.58	.0	2.14	...
23	342.2	7.30	1.20	...	.606	...	...	..	...	...	...
24	348.7	11.66	1.35	7.27	.821	6.99	.33	4.56	.0	2.54	...

TABLE II

RATES OF PRODUCT FORMATION IN THE PHOTOLYSIS OF 2-METHYLBUTANAL WITH FULL MERCURY ARC

Run	Temp., °C.	[C_4H_9CHO] M × 10^3	Rates, moles/l.-sec. × 10^8 CO	CH_4	C_2H_4	C_3H_6	C_4H_8	C_4H_{10}	C_8H_{18}
1	100.2	1.16	12.5	0.25	6.48	0.0	1.37	6.94	1.86
2	203.0	1.18	23.1	1.77	7.30	0.0	0.97	12.4	1.14
3	242.9	1.17	33.5	1.54	9.20	0.72	1.26	17.4	1.35
4	290.0	1.19	44.9	6.03	6.86	3.71	1.25	22.4	1.01
5	342.2	1.32	98.5	39.8	(13.5)	28.3	3.33	34.3	0.53

$C_4H_9 \rightarrow H + C_4H_8$, is unimportant up to 400°.[6] Probably the dominant reaction of the HCO radical at 350° is (5), and a rough estimate of the primary efficiency $\phi_I = 0.8$ is had from the value of Φ_{H_2} at high temperatures (see Fig. 2).

Primary process II is indicated by the temperature and intensity insensitivity of the quantum yield of ethylene; see Table I and Fig. 1. $\Phi_{C_2H_4}$ is 0.20 ± 0.03 in the temperature range 65–208°, and in experiments even at temperatures up to 350° the constancy of the yield continues within the larger experimental error of the determination at high temperatures. Process II is analogous to the ethylene-forming primary steps in *n*-butyraldehyde,[4] di-*n*-propyl ketone,[7] and methyl *n*-propyl ketone[8] photolyses. In every known case of photodecomposition of molecules containing a *n*-propyl chain adjacent to the light-absorbing carbonyl group, the general primary process II′ has been observed

$$CH_3CH_2CHRCOR' + h\nu \longrightarrow C_2H_4 + RCH_2COR' \quad (II')$$

Quantum yields of ethylene which are a measure of the primary efficiency of II′ are 0.17 ± 0.02 (25–150°) for *n*-butyraldehyde,[4] 0.20 ± 0.03 (65–208°) for 2-methylbutanal, and 0.21 ± 0.01 (113°) for di-*n*-propyl ketone[7] photolyses at 3130 Å. It is apparent that minor structure changes in R and R′ cause little, if any, change in the primary efficiency of II′. A detailed study of structural changes on ϕ_{II}' is under investigation in these laboratories.

A third primary process, III or III′, of minor importance ($\phi_{III} = 0.04$) is likely in view of the small, approximately constant quantum yield of CH_4 at temperatures below 200°.

$$CH_3CH_2CH(CH_3)CHO + h\nu \left\{ \begin{array}{ll} \longrightarrow CH_3 + C_3H_6CHO & (III) \\ \longrightarrow CH_4 + CH_3CH{=}CHCHO & (III') \end{array} \right.$$

Since it is estimated that $\phi_I = 0.8$, $\phi_{II} = 0.2$ and $\phi_{III} = 0.04$, the total primary quantum efficiency of decomposition appears to be near unity for 2-methylbutanal photolysis at 3130 Å.

Secondary Reactions.—The following reactions involving the decomposition and interactions of *sec*-butyl and formyl radicals are suggested for the quantitative explanation of the results

$$2CH_3CH_2CHCH_3 \left\{ \begin{array}{ll} \longrightarrow CH_3CH_2CH(CH_3)CH(CH_3){=}CH_2CH_3 & (1a) \\ \longrightarrow C_4H_8 + n\text{-}C_4H_{10} & (1b) \end{array} \right.$$

$$CH_3CH_2CHCH_3 \longrightarrow CH_3 + C_3H_6 \quad (2)$$

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(6) S. Bywater and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 172 (1951).

(7) C. R. Masson, THIS JOURNAL, **74**, 4731 (1952).

(8) A. J. C. Nicholson, *Revs. Pure Applied Chem.*, **2**, 174 (1952).

$$CH_3CH_2CHCH_3 + CH_3CH_2CH(CH_3)CHO \longrightarrow n\text{-}C_4H_{10} + CH_3CH_2CH(CH_3)CO \quad (3)$$

$$CH_3CH_2CH(CH_3)CO \longrightarrow CH_3CH_2CHCH_3 + CO \quad (4)$$

$$M + HCO \longrightarrow H + CO + M \quad (5)$$

$$HCO\ (+\ \text{wall}) \longrightarrow \text{Products not } H_2\ (+\ \text{wall}) \quad (6)$$

$$H + CH_3CH_2CH(CH_3)CHO \longrightarrow H_2 + CH_3CH_2CH(CH_3)CO \quad (7)$$

$$CH_3 + CH_3CH_2CH(CH_3)CHO \longrightarrow CH_4 + CH_3CH_2CH(CH_3)CO \quad (8)$$

The Decomposition of the *sec*-Butyl Radical.—In Fig. 1 it can be seen that Φ_{CH_4} (the blackened circles) and $\Phi_{C_3H_6}$ (triangles) increase simultaneously at temperatures above 250°. Within the rather large experimental error involved in C_3H_6 analysis, $\Phi_{CH_4} = \Phi_{C_3H_6}$. Reaction (2), the decomposition of the *sec*-butyl radical, accounts best for these results. It is probable that (8) is the major reaction of CH_3 in this system, since the other possible reaction products such as C_2H_6 and $(CH_3)_2CHCH_2CH_3$ could not be detected in the products. If it is assumed the I, III, (1a), (2) and (8) are the only steps leading to CH_4 and C_8H_{18}, then the relation (9) is derived.

$$\frac{k_2}{k_{1a}^{1/2}} = \frac{(\Phi_{CH_4} - \phi_{III})I_a^{1/2}}{\Phi_{C_8H_{18}}^{1/2}} = \frac{R_{CH_4} - R_{III}}{R_{C_8H_{18}}^{1/2}} \quad (9)$$

The function (9) was calculated from the quantum yield data of Table I for runs at temperatures above 230°. ϕ_{III} was taken as 0.04, the average Φ_{CH_4} for temperatures less than 200°. For the runs in which a direct measure of $\Phi_{C_8H_{18}}$ was not available, the value was estimated by interpolation from the data of Fig. 2. Function 9 was also calculated from the rate data for the two high temperature runs in Table II. R_{III} was taken as 0.25×10^{-8} mole/l. sec., the rate at 100°. An Arrhenius plot of these data is shown in Fig. 3. The inaccuracy in the analysis for products results in considerable scatter in the points, but the estimates based on data from the low intensity 3130 Å. runs (open circles) are in good agreement with those calculated from the runs at the high intensity (90-fold increase) of the full arc (blackened circles). The insensitivity of the function (9) to change in absorbed light intensity supports the proposed mechanism. The least squares treatment of all the data in Fig. 3 provides an estimate of the activation energy difference, $E_2 - E_{1a}/2 = 24$ kcal./mole and the pre-exponential factor ratio, $A_2/A_{1a}^{1/2} = 4.6 \times 10^4$ (mole/cc. sec.)$^{1/2}$. It is likely that $E_{1a}/2$ is near zero and thus $E_2 = 24$ kcal./mole. This is in good agreement with the value of $E_2 = 23$ kcal./mole estimated from the mercury photosensitized decomposition of *n*-butane.[6] If it is assumed that the kinetic estimates of $E_2 = 24$ and $E_{10} = 20$ kcal./mole[7,9,10] are correct, and that $E_{-2} = E_{-10}$, then

$$CH_3CH_2CH_2 \longrightarrow C_2H_4 + CH_3 \quad (10)$$

from standard enthalpy data we estimate that $D(n\text{-}C_3H_7\text{–}H) - D(sec\text{-}C_4H_9\text{–}H) = 6$ kcal./mole. The kinetic estimates of E_2 and E_{10} are reasonably consistent with estimates based on bond strengths and enthalpy data only if the "high" values of $D(n\text{-}C_3H_7\text{–}H) = 99$[11,12] and $D(sec\text{-}C_4H_9\text{–}H) = 93$ kcal./mole are used together with $D(CH_3\text{–}H) = 102$ kcal./mole and the pertinent enthalpy data. These give $E_2 = 26 + E_{-2}$ and $E_{10} = 22 + E_{-10}$. If E_{-2} and E_{-10} are near zero then these estimates are in fair agreement with the kinetic data for reactions (2) and (10). However, there is considerable direct and indirect evidence that supports higher values for the activation energy of radical addition to unsaturated molecules.[13] The best recent estimates of $E_{-2} = 6$ and $E_{-10} = 7$ kcal./mole lead to estimates of E_2 and E_{10} which are in serious disagreement with the kinetic estimates.[13d]

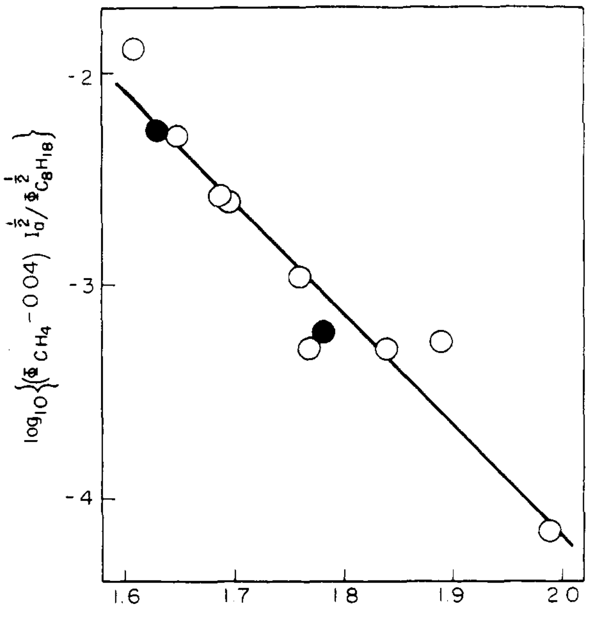

Fig. 3.—Arrhenius plot of the function theoretically equal to $k_2/k_{1a}^{1/2}$: the open circles are from data at 3130 Å.; the blackened circles are from experiments with the full mercury arc (about a 90-fold increase in the absorbed light intensity); the units of the function are (mole/l. sec)$^{1/2}$.

The ratio of pre-exponential factors, $A_2/A_{1a}^{1/2} = 4.6 \times 10^4$ (mole/cc. sec.)$^{1/2}$, found in this work appears to be inconsistent with the estimate of A_{-2} from the data of Mandelcorn and Steacie.[13d] If we assume A_{1a} is equal to or less than the collision number, $Z_{1a} = 2.0 \times 10^{14}$ cc./mole sec. ($\sigma_{C_4H_9} = 5.9$ Å., $T = 500$°K.), then $A_2 \leq 6.5 \times 10^{11}$ sec.$^{-1}$. This is in excellent agreement with the value of 10^{11} estimated by Trotman-Dickenson[14] from the data of Bywater and Steacie.[6] It may be estimated that $\Delta S°$ for reaction (2) = 13.8 e.u. with the standard state of 1 mole/cc. ($S°$ of *sec*-C_4H_9 assumed to be

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(11) C. H. Leigh and M. Szwarc, *J. Chem. Phys.*, **20**, 407 (1952).

(12) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

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(14) A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press Inc., New York, N. Y., 1955, p. 303.

76.8 e.u. at 1 atm., 25°).[15] By equating $\ln(A_2/A_{-2})$ to $\Delta S°/R$,[16,17] we estimate $A_{-2} \leq 6.5 \times 10^8$ cc./mole sec. The data of Mandelcorn and Steacie give $k_{-2} \cong 10^8$ at 177°, if the rate constant for methyl radical combination is assumed to be 5×10^{13}. If $E_{-2} = 6$ then these data suggest $A_{-2} \cong 10^{11}$ cc./mole sec. If however E_{-2} is actually near zero then $k_{-2} = A_{-2} \cong 10^8$, in reasonable agreement with the maximum (6.5×10^8) estimated from the present data. Obviously further experimentation is necessary to establish the origin of the inconsistencies in the estimates of the E_2, E_{-2}, A_2 and A_{-2}.

The present data show that the possible rearrangement reaction, *sec*-$C_4H_9 \rightarrow C_2H_5 + C_2H_4$, is an unimportant mode of homogeneous decomposition of the *sec*-butyl radical at temperatures up to 350°. It is very likely that ethane formation in the mercury-photosensitized decomposition of *n*-butane[6] originated entirely from the *n*-butyl radical decomposition, *n*-$C_4H_9 \rightarrow C_2H_5 + C_2H_4$. The improbability of the homogeneous decomposition of an alkyl radical (to form a smaller radical and an olefin) which requires a simultaneous H-atom shift, suggests that CH_4 formation in the mercury-photosensitized decomposition of butane[6] came from (2) alone. We have assumed this in comparing the present rate data with those obtained in the butane study.

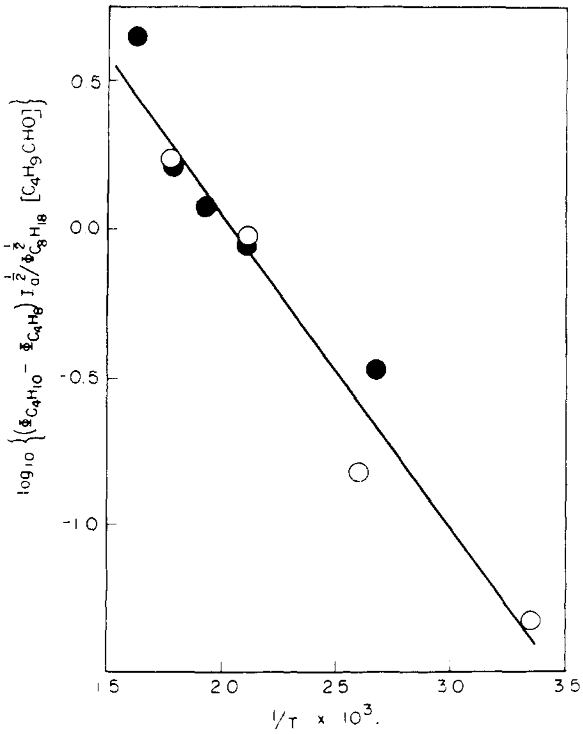

Fig. 4.—Arrhenius plot of the function theoretically equal to $k_3/k_{1a}^{1/2}$: the open circles are from data at 3130 Å.; the blackened circles are from experiments with the full mercury arc (about a 90-fold increase in the absorbed light intensity); the units of the function are (l./mole sec.)$^{1/2}$.

Hydrogen Abstraction by *sec*-Butyl Radicals.—If C_4H_{10} is formed only in reactions (1b) and (3) and C_8H_{18} in (1a), then the relation (11) should hold

$$\frac{k_3}{k_{1a}^{1/2}} = \frac{(\Phi_{C_4H_{10}} - \Phi_{C_4H_8})I_a^{1/2}}{\Phi_{C_8H_{18}}^{1/2}[C_4H_9CHO]} = \frac{R_{C_4H_{10}} - R_{C_4H_8}}{R_{C_8H_{18}}^{1/2}[C_4H_9CHO]} \tag{11}$$

In Fig. 4 is shown an Arrhenius plot of the function (11), calculated from the quantum yield data of Table I (open circles) and the rate data of Table II (blackened circles). Within the experimental error, the two sets of data obtained at greatly different intensities determine the same straight line, as is required by (11). The least squares line through all the points gives $E_3 - E_{1a}/2 = 4.9$ kcal./mole and $A_3/A_{1a}^{1/2} = 4.8 \times 10^3$ (cc./mole sec.)$^{1/2}$. If we again assume $A_{1a} \leq Z_{1a} = 2.0 \times 10^{14}$ cc./mole sec., then $A_3 \leq 6.8 \times 10^{10}$ cc./mole sec.; this corresponds to a collision theory steric factor $P_3 \leq 3 \times 10^{-4}$, the usual order of magnitude of the P-factors for the H-abstraction reactions of the other simply alkyl radicals.

Disproportionation and Combination of the *sec*-Butyl Radical.—The ratio of the rate of formation of C_4H_8 to that of C_8H_{18} at 25° is essentially independent of the light intensity: 0.68 at the low intensity of 3130 Å. radiation and 0.61 at the high intensity of the full arc (obtained by extrapolation of the data of Table II). The facts are consistent with the formation of C_4H_8 and C_8H_{18} in reactions (1a) and (1b). Since these reactions are favored by high radical concentrations provided by high light intensities, the experiments at full arc give the highest rates and thus the most accurate data concerning these reactions. The rate data of runs 1, 2 and 3 of Table II and run 2 of Table I are considered most reliable and were used to prepare the Arrhenius plot of $R_{C_4H_8}/R_{C_8H_{18}}$ in Fig. 5. From

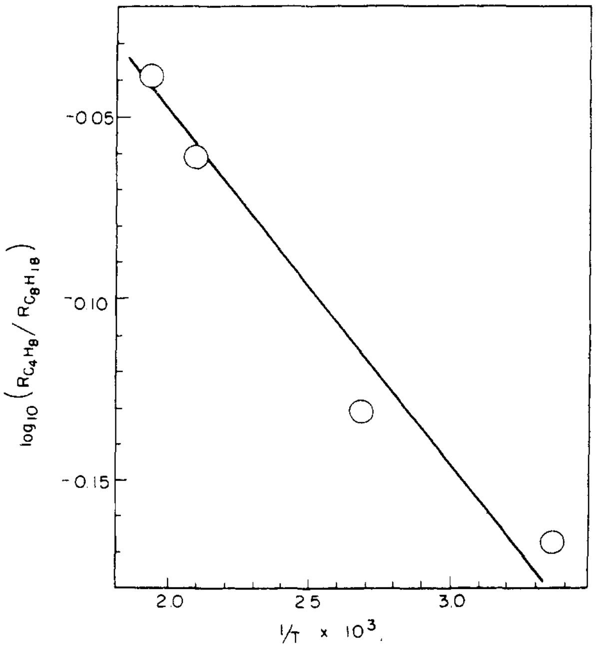

Fig. 5.—Arrhenius plot of the function theoretically equal to k_{1b}/k_{1a}: data are from experiments with the full mercury arc.

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this it is estimated that $E_{1a} - E_{1b} = 0.5$ kcal./mole, and $A_{1a}/A_{1b} = 1.4$. The relatively large ratio of $k_{1a}/k_{1b} = 0.61$ at 25° is consistent with the observation[4,18] that secondary free radicals have a significantly higher ratio of the rate of disproportionation to that of combination than the primary radicals. This may reflect the increased probability of the abstraction reaction for the secondary radicals (there are more H-atoms per radical which can be abstracted and lead to an olefin product), and/or the decreased rate of combination of the more sterically hindered radical.

The Mechanism of Hydrogen Formation.—For runs at a given temperature Φ_{H_2} is approximately independent of the absorbed light intensity for consecutive experiments with similar wall conditioning; compare Φ_{H_2} from runs 10 and 12, and 14 and 15 of Table I. The increase in Φ_{H_2} with temperature (Fig. 2) suggests the increasing importance of formyl radical decomposition at high temperatures. Pronounced variation in Φ_{H_2} was found in duplicate experiments separated by an extended period of photolysis. All of these facts are consistent with the formation of hydrogen in the sequence I, (5), (6) and (7). It is likely that the effectiveness of the wall for reaction (6) was altered by polymer formation; in general the cleaner the cell the higher was Φ_{H_2}, and presumably the less effective the wall for reaction (6). Compare runs 18, 19, and 20, and 23 and 24 in Table I. The yields of hydrogen are too variable in this system to provide a meaningful estimate of the activation energy of the hydrogen forming reactions.

The Configuration of Alkyl Free Radicals.—The results show that the photolysis of 2-methylbutanal is a good source of *sec*-butyl radicals. The *sec*-butyl radical is of special interest since it is the simplest alkyl radical which may contain an asymmetric carbon atom. A study of the vapor phase, iodine-inhibited photolysis of 2-methylbutanal is in progress in these laboratories. It is hoped that the information gained concerning the vapor phase reaction between the *sec*-butyl radical and molecular iodine may aid in the choice between the possible planar and tetrahedral configurations of the simple alkyl radicals.

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[CONTRIBUTION FROM THE BUREAU OF MINES, PETROLEUM AND OIL-SHALE EXPERIMENT STATION]

Gaseous Decomposition Products Formed by the Action of Light on Organic Sulfur Compounds[1]

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Exposures of 30 highly purified sulfur compounds to a mercury-vapor light under identical conditions produced gaseous decomposition products that were analyzed mass spectrometically. The experiments included 13 thiols, 8 sulfides, 3 cyclic sulfides, 2 disulfides and 4 thiophenes. Decompositions, as measured by the gaseous products, ranged from 0.004 to 3.0 mole %. Thiols showed greater amounts of decomposition than the other types of sulfur compounds and gave hydrogen as the main product. Sulfides and disulfides yielded, as the predominant product, a saturated hydrocarbon corresponding to the smallest alkyl radical attached to the sulfur. Thiophenes gave hydrogen and hydrogen sulfide. These experiments show that the sulfur compounds studied must be protected from light to maintain high purity.

The action of light on highly purified organic sulfur compounds prepared by American Petroleum Institute Research Project 48 was investigated as part of a study of the stability of these compounds. The compounds, which are used for instrument calibration and research studies, often are stored for considerable periods before use, hence it is desirable to obtain information about their stability during storage, both in the dark and in the light. Work previously reported from this Laboratory[2] on 20 of the compounds has shown that no decomposition occurs upon dark storage. Only 6 of these compounds—thiacyclobutane, 2,3-dithiabutane, 3,4-dithiahexane, 2-methylthiophene, 3-methylthiophene and benzo[b]thiophene—showed instability when stored in sunlight for 1 year. These decompositions were estimated by freezing-point purity measurments,[3] which detect only the decomposition products remaining as impurities in the liquid.

Recently, interest was directed to the decomposition products that might not be detected by the methods previously used. Thirty highly purified sulfur compounds were exposed to artificial light and the gaseous decomposition products were analyzed by mass spectrometric methods. The technique developed has particular value when the amount of decomposition is small and the purity of the starting material is great enough so that the impurities may be assumed not to be responsible for the products. Some insight into the mechanism of the reaction may be drawn from the results.

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[1] This work was done as part of API Research Project 48A on the Synthesis, Properties and Isolation of Sulfur Compounds of Petroleum carried out by the Bureau of Mines at Laramie, Wyo., and Bartlesville, Okla. The paper was presented before the Division of Petroleum Chemistry, American Chemical Society, Minneapolis, Minn., Sept. 1955.

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