needles, m. p. 208–209° (cor.); yield, 0.8 g., from 1 g. of the anil.

Anal. Calcd. for $C_{28}H_{26}N_2O_2$: C, 79.6; H, 6.1; N, 6.6. Found: C, 79.2; H, 6.4; N, 6.4.

The oxime group is placed on carbon no. 4, because it is believed that the reaction proceeds through a displacement of the anil group by the hydroxylamine, rather than by a condensation with the free carbonyl group in position no. 5, the latter being sterically hindered.

3-Benzalaminoretene (VIII).—A solution of 1 g. of 3-aminoretene in 30 cc. of absolute ethanol was refluxed for three hours with 2 cc. of freshly distilled benzaldehyde. The mixture slowly turned red during the course of the reaction. The solution was cooled and allowed to stand overnight in the refrigerator. This precipitated the benzalamine as clumps of yellow crystals, which were dissolved in hot absolute methanol, cooled slowly to room temperature, and again allowed to stand overnight in the refrigerator. The benzalaminoretene came down as clusters of shining yellow blades, which were dried for a week in a vacuum desiccator. The compound was unstable, and even on short contact with moist air, the odor of benzaldehyde became apparent, m. p. 88–89° (cor.); yield, 0.6 g.

Anal. Calcd. for $C_{25}H_{23}N$: C, 89.0; H, 6.8. Found: C, 88.5; H, 6.9.

Summary

1. 3-Aminoretene is more conveniently prepared from β-3-retoylpropionic acid than from 3-acetylretene.

2. From this amine, a retopyridine (naphthoquinoline) has been synthesized by the Skraup reaction, and a retopicoline (naphthoquinaldine) by the Doebner–von Miller reaction.

3. The classical Doebner reaction, for the production of cinchoninic acids, converts the aminoretene into a diketopyrrolidine anil, without the formation of appreciable quantities of either benzalaminoretene or the expected cinchoninic acid derivative.

NEW YORK, N. Y. RECEIVED NOVEMBER 29, 1940

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL GASOLINE CORPORATION]

The High-Temperature Photolysis of Acetone and the Action of Free Methyl Radicals on Propane

BY AUGUSTINE O. ALLEN

Acetone illuminated by light of wave lengths between 2000 and 3200 Å. is known to break up cleanly to free methyl and acetyl radicals.[1] This reaction provides a convenient source of free methyl radicals for the study of reactions induced by them over the temperature range 150–400°. For inducing oxidation reactions especially, acetone has a great advantage over such sources as methyl iodide and dimethylmercury, in that no reactive oxidation inhibitors are simultaneously produced from the source to complicate the reaction. It is well known, however, that at these temperatures a complicating reaction occurs in the acetone photolysis, leading to the formation of methane.[2] In the present work, studies on the products and mechanism of this reaction are described. Also, the use of acetone as a source of free methyl radicals is illustrated by some data on the products obtained by illumination of mixtures of acetone and propane.

Experimental

A 500-watt high-pressure Hanovia mercury arc lamp was used for the light source; a starting switch provided with the lamp allowed some variation of the intensity. The cylindrical fused quartz reaction vessel (capacity about 200 cc.) was placed in a hand-regulated aluminum block furnace. In a slit in the side of the furnace, between light source and reaction vessel, was placed a quartz cell through which flowed a 0.02 *N* solution of acetic acid to filter out wave lengths below 2000 Å. Acetone vapor and C. P. propane (warranted 99.9% pure) were introduced into a 2-liter storage bulb, then drawn into the reaction vessel as needed. No stopcocks were used in the filling and reaction systems, their place being taken by Hoke packless diaphragm-type valves of brass, sealed into the glass system by picein wax.

The reaction products were withdrawn by means of a hand-operated Toepler type pump, consisting simply of a vertical glass cylinder connected to a mercury leveling bulb, with a three-way stopcock at the top. For runs in which only the permanent gas fraction was analyzed, a liquid-air trap was inserted next to the reaction vessel, and the uncondensed gas (which would contain substantially no ethane) was pumped by the hand Toepler into an Orsat apparatus. To obtain a more complete analysis, recourse was had to a fractionation apparatus patterned after that of Ward.[3] Through a series of five small traps, which

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(1) (a) Gorin, *J. Chem. Phys.*, **7**, 256 (1939); (b) Herr and Noyes, THIS JOURNAL, **62**, 2052 (1940).

(2) (a) Leermakers, *ibid.*, **56**, 1879 (1934); (b) Winkler, *Trans. Faraday Soc.*, **31**, 761 (1935); (c) Akeroyd and Norrish, *J. Chem. Soc.*, 890 (1936); (d) Taylor and Rosenblum, *J. Chem. Phys.*, **6**, 119 (1938).

(3) Ward, *Ind. Eng. Chem., Anal. Ed.*, **10**, 169 (1938).

could be maintained at constant (±1°) low temperatures, as described by him, the reaction products were allowed to distil fractionally at low pressures, the vapors being divided into five fractions: C_1 (non-condensable), C_2 (ethane), C_3 (propane), C_4 (butane) and heavier. It was found that best results were obtained with separation of fractions at pressures of 0.02 mm. for the C_1-C_2 separation and 0.001 mm. for the others, which are lower than the pressures recommended by Ward. It was also found that in the C_3-C_4 separation the fourth trap should be kept 2° higher than he recommends. Results on the analysis of synthetic mixtures are shown in Table I. It is seen that as the separation pressures are reduced, the C_2 and C_3 fractions increase toward the true values, and that the fractionation is accurate to within 1%.

TABLE I

PERCENTAGE ANALYSES OF SYNTHETIC MIXTURES

Sepn. press.	0.25 and 0.1 mm.		0.01–0.03 mm.		0.02 and 0.001	
	Taken	Found	Taken	Found	Taken	Found
Air	30.5	30.1	23.6	23.6	44.1	45.0
C_2H_4	26.7	26.0	30.4	29.4	30.0	29.7
C_3H_8	21.0	18.4	21.7	20.6	0.0	−0.1
C_4H_{10}	21.9	24.1	23.2	24.3	.0	.1
Me_2CO	0.0	0.1	1.2	Undetd.	25.8	Undetd.

The fractions were measured in the buret shown in Fig. 1. The apparatus is calibrated so that the volume occupied by the gas is known from the height of the mercury in the tube T_1, while the difference in level between T_1 and T_2 gives simultaneously the pressure. The product pv is used to measure the amount of gas. By varying the height of the leveling bulb, a number of readings (in practice, three) can be taken on the same sample at different pressures, thus increasing the accuracy. This buret was found very convenient for measuring quantities of gas varying over the very wide range of 1 to 400 ml. at standard pressure, and the presence of condensable vapors such as acetone was no drawback, as the pressure may be kept as low as desired.

After each run, the reaction vessel was cut down, and a deposit was always found to exist on the wall; though generally invisible, it was manifested by the fact that water would not wet the surface. The vessel was cleaned with nitric–chromic acid and heated in an oxy-gas flame to bright red heat before sealing it back on for the next run. Less deposit was apparent in the experiments with propane than in those with acetone alone.

To determine the nature of the condensable products in the high-temperature acetone photolysis, a flow system was used. Acetone vapor passed through an inlet tube extending to within 1 cm. of the bottom of the reaction vessel; on emerging, the gas was passed through two traps at −78°, then went either to the pumping system, which included a regulator for maintaining a constant pressure (about 30 mm.) in the traps, or to a liquid-air trap and thence to the gas-collecting system and Orsat apparatus. The rate of flow was regulated by the valves on either side of the reaction system, and was determined by noting the rate of evaporation of liquid acetone from the graduated vessel used as a source. At the end of the run, the traps were cut down, and the bulk of the acetone stripped from the product in an ordinary fractionating column packed with glass beads; the residue was then distilled through a special vacuum-jacketed fractionating column designed for minimum holdup, the fractionation occurring simply in the unpacked annular space between the wall and the column and a central rod. The efficiency of this column was very sensitive to the rate of boiling, and the distillation had to be made slowly and with great care; a test mixture of acetone and carbon tetrachloride was distilled with an intermediate fraction of 0.6 ml. between the distillation flats.

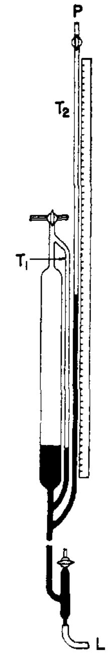

Fig. 1.—Gas buret: L, connection to leveling bulb; P, to vacuum pump.

For the acetone–propane mixtures, no flow run was made, but the products of 27 successive static runs were condensed in liquid nitrogen and the condensable portions combined and distilled in a Podbielniak column.[4] The reaction vessel was not cleaned between runs in this case, yet no visible deposit was formed, while at the end of the pure acetone flow runs a dark brown varnish-like film, insoluble in boiling acetone, was seen.

Results

Pure Acetone.—The permanent gas from the photolysis of pure acetone was analyzed for carbon monoxide, and the remainder was assumed to be methane in view of the results of previous investigators and the absence of hydrogen and ethylene in the products from propane–acetone mixtures (see below). Table II shows the ratio of methane to carbon monoxide obtained under various conditions. In these runs the time of illumination was twelve minutes; about half the acetone was decomposed. The fifth column of the table gives the initial rate of pressure rise divided by the initial pressure; the figures are somewhat greater at the lower pressures, showing that an appreciable

TABLE II

METHANE AND CARBON MONOXIDE FROM ACETONE

Expt.	T, °K.	P_0, mm.	Light intensity	$\frac{dP_0}{P_0\,dt}$ (min.$^{-1}$)	$\frac{CH_4}{CO}$	$\frac{CH_4}{CO}$ av.
A-8	520	94.5	Low	0.074	0.151	0.164
A-9	521	51.5	Low	.096	.170	
A-10	522	160.4	Low	.062	.198	
A-11	522	131.3	High	.092	.138	
A-15	549	160.9	Low	.052	.259	.243
A-16	550	154.4	High	.104	.228	
A-12	567	120.7	High	.100	.294	.277
A-13	567	112.5	Low	.068	.248	
A-14	565	103.8	Low	.072	.290	
A-17	619	147.2	Low	.066	.529	.529

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[4] The author is indebted to Mr. H. R. Neal for carrying out this distillation.

fraction of the light is absorbed in the vessel; this is undoubtedly due to multiple reflections of the light from the walls of the aluminum container. This column shows that the ratio of "high" to "low" intensity was not more than two. The temperatures are reported as 4° higher than the observed furnace temperature, as a pressure drop on turning off the light was found corresponding to about this degree of heating of the gas by the radiation.

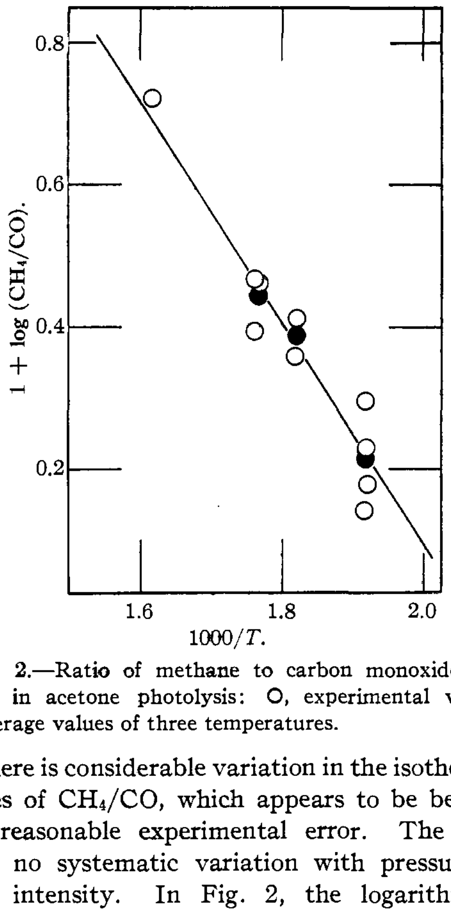

Fig. 2.—Ratio of methane to carbon monoxide produced in acetone photolysis: O, experimental values; ●, average values of three temperatures.

There is considerable variation in the isothermal values of CH_4/CO, which appears to be beyond any reasonable experimental error. The data show no systematic variation with pressure or light intensity. In Fig. 2, the logarithm of CH_4/CO is plotted against $1/T$; the average values (from the last column of Table II) fall near a straight line of slope corresponding to an "activation energy" of 7100 cal.; Taylor and Rosenblum[2d] find 8600 cal. from four experiments; the difference is to be expected in view of the irreproducibility of the reaction.

Table III gives the results of a series of runs in which complete product fractionations were carried out. The amount of carbon monoxide present has been estimated by multiplying the amount of permanent gas by the percentage of carbon monoxide it would be expected to contain at the temperature of the experiment, as read from the line in Fig. 2. In Experiment A-7, the three condensable fractions were taken off and measured together. The high value for "C_4" in Experiment A-6 is probably in error. The last column shows that the total moles of hydrocarbon formed are equal to the moles of carbon monoxide within experimental error. That the shorter time runs show no difference from the others demonstrates that the bulk, at least, of the methane does not arise merely from secondary reactions involving the products of the main reaction.

The formation of methane must be balanced stoichiometrically by the production of some oxygen-containing compound. Tests for ketene, acetonylacetone and acetylacetone were negative, and the flow system was set up to produce sufficient quantity of the product to allow identification. In the first flow run (time 1900 min., 102.2 ml. acetone passed, average time for acetone to pass through reaction vessel 0.79 min.) the fractionating column used was unable to separate the compound in a sufficiently pure state for identification, but it was found to boil about 80° and to possess an odor similar to acetone but somewhat sharper; these properties suggested methyl ethyl ketone. The product from a second flow run (time 3970 min., 187.5 ml. acetone passed, average time in reaction vessel, 1.16 min.) was

TABLE III

FRACTIONATION ANALYSIS OF GASEOUS PRODUCTS FROM PURE ACETONE

Expt.	T, °K.	P_0, mm.	Time, min.	$\frac{CH_4}{CO}$ (graph)	$\frac{C_2}{CO}$	$\frac{C_3}{CO}$	$\frac{C_4}{CO}$	$\frac{CH_4 + C_2 + C_3 + C_4}{CO}$
A-1	481	111.5	12	0.093	0.918	0.024	0.005	1.040
A-2	520	156.0	12	.163	.767	.053	.010	0.993
A-3	519	140.8	4.5	.161	.820	.018	.008	1.007
A-4	520	164.0	12	.163	.709	.054	.010	0.936
A-5	521	150.2	12	.164	.782	.066	.010	1.022
A-6	518	137.1	4.5	.159	.818	.045	.047	1.069
A-7	577	150.0	12	.322	...	..	...	1.007
							Av.	1.011

distilled through an improved column, and a 0.4-ml. cut was obtained, estimated to contain only 10–15% of acetone. This material was treated with 2,4-dinitrophenylhydrazine[5] and the derivative was purified by recrystallization from alcohol. The derivative of methyl ethyl ketone is difficult to purify, even the hydrazone from a supposedly pure sample of ketone requiring five recrystallizations. The derivative from the product after thirteen recrystallizations melted at 109–111°; its mixture with pure methyl ethyl ketone derivative (m. p. 116°) melted at 112–114°. This was taken as good evidence of identification.

The composition of permanent gas samples taken during the flow runs is shown in Table IV. The proportion of methane was higher than in static runs made at the same temperature, and increased as the light intensity (as shown by the rate of gas formation) decreased. This decrease in intensity was caused partly by the formation during the run of the brownish wall deposit, and partly by a deterioration of the mercury arc lamp which was especially marked in the second run. There is thus some dependence of methane yield on intensity; and the wall deposit probably also catalyzes methane formation.

TABLE IV

METHANE AND CARBON MONOXIDE FROM FLOW RUNS

Run	Time from start, hr.	Temp., °K.	Rate of gas formation, ml./min.	CH_4/CO
I	19	654	0.92	0.39
	24	657	. .	.44
	31	655	.76	.42
II	42	654	.37	.62
	50	654	.28	.62
	57	654	.27	.67

Propane–Acetone Mixtures.—The results of product fractionations of a series of runs at different temperatures are shown in Table V. The propane:acetone ratio was 2:1, and the time of illumination was twelve minutes; about half the acetone was decomposed. The propane used was obtained by subtracting from the amount taken into the reaction vessel, the amount found in the products. Hydrogen and unsaturated compounds were shown to be absent by testing the products of Experiments B-5 and B-16 with copper oxide at 290° and with bromine water; paraffins and carbon monoxide are the only gaseous products.

The Podbielniak distillation curve of the combined products of twenty-seven runs is shown in Fig. 3. The compounds up to propane were taken off at atmospheric pressure; the heavier, at 100 mm. In the figure are indicated the points on the millivolt temperature scale of the apparatus at which various pure compounds distil under the appropriate pressure, as established by distillations of synthetic mixtures. The methane, ethane, propane, isobutane and normal butane plateaus are sharply defined, and the absence of ethylene, propylene, and butenes is obvious. Some substances are present boiling between butane and acetone, probably pentanes. The presence of residual acetone prevents detection of hexanes or heavier fractions. Table VI gives the amounts of the various substances present, the cut points being obtained by the equal area method except the butane–pentane break, which was set arbitrarily. The higher ratio of butane to ethane in Table VI than in Table V may be due to loss of ethane in the process of separating the noncondensable gases for the sample for Podbielniak analysis, or to some butane having remained dissolved in the residual acetone during the fractionation in the Ward apparatus.

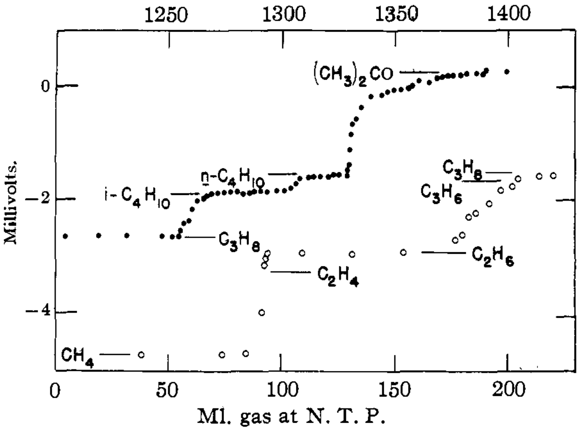

Fig. 3.—Podbielniak distillation of products from propane–acetone mixture. The open circles and figures on the lower margin refer to the first part of the distillation, made at atmospheric pressure; the solid circles and figures on the upper margin refer to the last part, made at 100 mm. pressure. The horizontal lines show the temperatures at which the indicated pure compounds distil over.

Discussion

It is natural to assume that the methane formed in high-temperature acetone photolysis arises from the action of methyl radicals on acetone molecules; the acetonyl residue then combines with

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(5) C. F. H. Allen, THIS JOURNAL, **52**, 2955 (1930).

TABLE V

REACTION PRODUCTS (MILLIMOLES) FROM PROPANE–ACETONE MIXTURE

Expt.	T, °K.	P_0, mm.	Taken Acetone	 C_3H_8	Found $CH_4 + CO$	 C_2H_6	 C_4H_{10}	C_3H_8 used	$\frac{2 \times C_3H_8 \text{ used}}{C_2H_6 + CH_4 + CO}$
B-1	527	208.4	0.648	1.299	0.519	0.279	0.040	0.050	0.125
B-4	540	149.8	.466	0.946	.368	.188	.016	.036	.129
B-2	564	153.3	.460	.922	.414	.159	.022	.048	.167
B-3	572	145.9	.434	.868	.392	.132	.038	(.062)	(.237)
B-5	583	138.4	.405	.822	.373	.128	.039	.045	.180
B-6	610	127.0	.363	.737	.370	.105	.022	.0595	.250

TABLE VI

RESULTS OF PODBIELNIAK ANALYSIS

Substance	Ml. gas at N. T. P. Cut point	 Amount present
CH_4 and permanent gas	91	91
C_2H_6	188	97
C_3H_8	1261	1073
i-C_4H_{10}	1309	48
n-C_4H_{10}	1333	24

another methyl to form methyl ethyl ketone. A simple mechanism consistent with the present results, and with those of Gorin,[1a] is given by the following equations, where r stands for reaction rate and x_0, x_1, and x_2 are, respectively, the concentrations of acetone, acetyl, and methyl.

$$\begin{array}{rcll}
CH_3COCH_3 + h\nu & = & CH_3 + COCH_3 & r_0 = k_0x_0 \\
COCH_3 & = & CO + CH_3 & r_1 = k_1x_1 \\
COCH_3 + CH_3 & = & C_2H_6 + CO & r_2 = k_2x_2x_1 \\
CH_3 + CH_3COCH_3 & = & CH_4 + CH_2COCH_3 & r_3 = k_3x_2x_0 \\
CH_3 + CH_2COCH_3 & = & C_2H_5COCH_3 & r_4 = r_3
\end{array}$$

The first equation assumes that the light absorbed is, for a given intensity, proportional to the acetone pressure; this is close enough to the truth for the present purposes. A reaction between methyl radicals to give ethane is omitted because its inclusion would create a pressure dependency for the methane production; Burton, Taylor and Davis[6] have shown this reaction to be unimportant under conditions similar to those found here.

If we let B represent the methane–carbon monoxide ratio in the products, then $B = r_3/(r_1 + r_2) = r_3/r_0$. Applying the usual steady-state method, we find $(1 - B)/B^2 = k_0k_2/k_1k_3$. Thus B should be independent of acetone pressure, and should increase but slightly as the light intensity decreases, in agreement with the experiments.

The irreproducibility of the methane formation, and its apparent catalysis by the wall deposit, strongly suggest that the reaction of methyl with acetone occurs on the vessel wall. The acetonyl radicals produced would then remain fixed to the wall until struck by another methyl radical, with methyl ethyl ketone resulting from this encounter. This picture explains why the acetonyl radicals do not dimerize to acetonylacetone. Rice, Rodowskas and Lewis[7] found that methyl radicals from the pyrolysis of dimethylmercury react with acetone to yield diacetonyl; there the reaction is presumably homogeneous. It is difficult to say why the homogeneous reaction should occur in one case and not in the other; either the radicals from dimethylmercury pyrolysis possess more energy than those from acetone photolysis, or the activated dimethylmercury molecules react with acetone directly.

Spence and Wild[8] found that, at 60°, the production of methane in the acetone photolysis increased markedly with increasing pressure and decreasing light intensity. The difference from the results at high temperatures is not surprising, as it is known[1] that the reactions of the acetyl radical, and consequently the whole reaction mechanism, are quite different in the two temperature regions.

The small amounts of propane and butane formed in the pure acetone photolyses must be due to a reaction of methyl radicals on the primary product, ethane, to produce free ethyl, which will then react with methyl, with acetyl, or with itself to give the observed hydrocarbons.[9] The overall chemical changes occurring will then be given by the equations

$$\begin{array}{rcll}
CH_3COCH_3 & = & C_2H_6 + CO & (1) \\
2CH_3COCH_3 & = & CH_4 + CO + C_2H_5COCH_3 & (2) \\
2CH_3COCH_3 & = & 2CO + CH_4 + C_3H_8 & (3) \\
3CH_3COCH_3 & = & 3CO + 2CH_4 + C_4H_{10} & (4)
\end{array}$$

Thus the total number of moles of hydrocarbon and of carbon monoxide formed should be the same, as was in fact observed.

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[6] Burton, Taylor and Davis, *J. Chem. Phys.*, **7**, 1080 (1939).

[7] Rice, Rodowskas and Lewis, THIS JOURNAL, **56**, 2497 (1934).

[8] Spence and Wild, *J. Chem. Soc.*, 352 (1937).

[9] Hydrocarbon radicals larger than methyl can presumably combine more readily in the gas phase, by reason of their greater number of degrees of freedom.

A similar reaction must occur in the experiments with added propane; the free methyl reacts with propane to give methane and a propyl or isopropyl radical. It is interesting that at the temperatures used there is no decomposition of the propyl radical to give unsaturated compounds. Since the amount of propane reacting is small compared to the amount of acetone decomposed, the methyl and acetyl radicals are the most abundant; and the propyl (and isopropyl) radicals will disappear chiefly by reaction with methyl, and probably also with acetyl, to give butane (and isobutane). The chief over-all reactions taking place will then be (1) and (2) above, together with

$$CH_3COCH_3 + C_3H_8 = CO + CH_4 + C_4H_{10} \quad (5)$$

Each of these three modes of reaction arises from a different reaction of the radicals formed from acetone. If they react with one another, the result is (1); if they react with acetone, we have (2); and if they act on propane, (5) results. The amount of acetone decomposing to free radicals should be equal to half the sum of the methane, ethane, and carbon monoxide formed; and the fraction of radicals reacting with propane should be given by dividing this quantity into the amount of propane used. The experimental values of this fraction are given in the last column of Table V, and in Fig. 4 its logarithm is plotted against $1/T$. (Experiment B-3, in which the propane determination is obviously in error, is omitted from the plot.) The deviations of the points from the line drawn in the figure are well within the probable experimental error.

The greater reproducibility of the propane reaction and the smallness of the wall deposit, as compared with the pure acetone reaction, indicate that the reaction of methyl radicals with propane is largely homogeneous. The positive temperature coefficient of the reaction of propane with methyl radicals (the line of Fig. 4 corresponds to an "activation energy" of 5200 cal.) is consistent with the idea that a homogeneous methyl–propane reaction is competing with a methyl–acetone reaction which, being heterogeneous, has a lower temperature coefficient.

Steacie and Dewar[10] have shown qualitatively that the hydrogens on the secondary carbon atom in propane are more weakly bound than those on the primary. Smith and Taylor[11] find that the temperature coefficient of the reaction with free methyl is greater for hydrocarbons containing only primary carbon atoms than for those containing secondary carbon, and give 2800 cal. as the difference between the energies of the two types of C–H binding. The present work provides a direct measurement of the difference in activation energy for removing hydrogen from primary and secondary carbon atoms in the same compound. If the radicals attack the secondary linkage, isopropyl is formed, which yields isobutane; attack on the primary yields normal butane. Table VI shows that the ratio of isobutane to butane is 2:1. As there are three times as many primary as secondary hydrogens, the relative probabilities of attack must be 6:1. At 579°K., the average temperature of the 27 runs which gave the product, this ratio corresponds to a difference of 2060 cal. in activation energy—in good agreement with Smith and Taylor's value.

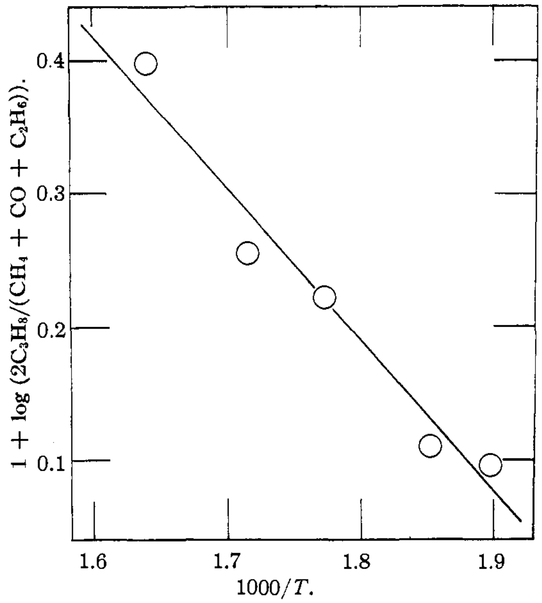

Fig. 4.—Fraction of the free radicals produced which react with propane.

The pentanes apparently present here must be secondary products arising from the action of methyl radicals on the butanes. This reaction probably does not appreciably affect the relative proportions of iso and normal butanes, as isobutane, with one tertiary and no secondary carbon, should react at about the same rate as normal butane, with four secondaries; this supposition is confirmed by the data of Smith and Taylor for this temperature region.[12]

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[10] Steacie and Dewar, *J. Chem. Phys.*, **8**, 571 (1940).

[11] Smith and Taylor, *ibid.*, **7**, 390 (1939).

[12] See Fig. 3 in Ref. 11.

Summary

1. The high-temperature photolysis of acetone has been shown to yield methyl ethyl ketone. The yield of methane under various conditions was studied. The results are consistent with a simple mechanism involving a wall reaction between free methyl radicals and acetone.

2. Propane was found to be attacked by free radicals from photolyzing acetone. The products contained no unsaturated hydrocarbons, and it is concluded that the free propyl and isopropyl radicals are stable at 610°K. and below. From the butane–isobutane ratio in the products, it is estimated that the activation energy for removal of a hydrogen from the secondary carbon atom is 2060 cal. less than for a similar attack on a primary linkage.

Detroit, Michigan Received November 29, 1940

[Contribution from the Chemical Laboratory of the University of California]

Magnetism and the Third Law of Thermodynamics. Magnetic Susceptibility, Adiabatic Change of Temperature on Magnetization and Heat Capacity of $NiSO_4 \cdot 7H_2O$[1]

By J. W. Stout[2] and W. F. Giauque

Among the more important problems arising in the use of the third law of thermodynamics for determining chemical equilibria is the one concerned with the multiple electronic states which persist in many solids at low temperatures. The commonest indication of this situation is found in the paramagnetism of such compounds. When the magnetic susceptibility changes with temperature one may infer that the electronic system has not reached a sufficiently low temperature so that substantially all of the atoms are in the lowest electronic state. Unless heat capacity measurements on such a substance are carried to sufficiently low temperatures, they may give no indication of the entropy associated with the magnetic system. The absence of a temperature coefficient in the magnetic susceptibility may be taken to indicate that the electronic contribution to the total entropy has been lost.

The magnitude of the magnetic susceptibility and its temperature coefficient usually give an indication of the type of system which exists in the solid but will not in general give the number of states and thus permit a calculation of the entropy. We have in mind the susceptibility as determined with a sample of powdered substance since this is most easily measured and usually provides the only data available in the few compounds where any data exist. In the case of a powder it is possible for more than one situation to give the same susceptibility and thus the entropy cannot always be inferred from such incomplete magnetic data alone.

A sufficiently detailed study of the axial susceptibilities of a perfect crystal as a function of temperature should often enable the calculation of the entropy associated with the magnetic system without the necessity of actual measurements at temperatures low enough to remove the entropy concerned. It is often possible to predict the number of electronic states to be expected in the solid state at higher temperatures but at very low temperatures it remains for experiment to decide if one or more of the upper levels is practically unoccupied.

One can obtain the entropy of such substances from heat capacity data alone but it will often require measurements at temperatures below 1°K. In fact it was this problem of determining the entropy in such systems which led to the invention of the adiabatic demagnetization process of producing very low temperatures in this Laboratory. However, many experimental difficulties still remain to be overcome in the temperature range below 1°K. before the accuracy customary at higher temperatures is attained.

In this paper we will discuss measurements of the heat capacity, magnetic susceptibility and related quantities for nickel sulfate heptahydrate from 1 to 15°K. This case is of unusual interest in illustrating the effects discussed above because the energy separations in the electronic states are large enough to cause the more interesting behavior to occur above 1°K. At the same time

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(1) Presented before the Boston Meeting of the American Chemical Society, Sept. 1939.

(2) Now at the Massachusetts Institute of Technology.