and of sufficient size that it may be regarded as spherical. Introducing elliptical coordinates with the smaller ellipsoid as the reference surface for which the coordinate $\xi = 0$, the larger ellipsoid will be the surface $\xi = \Xi$, $\Xi >> 1$. The remainder of space will be of permittivity unity, and the inner ellipsoid will contain a uniform fixed polarization of magnitude $\vec{p}$ per unit volume, directed along the principal semi-axis of length a. A boundary condition at $\xi = 0$, then, is that $\epsilon(\partial\psi/\partial n)$ will suffer a discontinuity of magnitude $-\vec{p}\cdot n$, where $\hat{n}$ is a unit vector normal to the bounding surface. The remaining boundary conditions result from the continuity everywhere of ψ and its regularity at infinity, and continuity of $\epsilon(\partial\psi/\partial\hat{n})$ at the outer boundary surface.

The boundary value problem just described may be solved by standard methods.[20] It is found that the potential outside the specimen assumes the form, in the limit of large Ξ

$$\psi = \left(\frac{3}{\epsilon + 2}\right)\left(\frac{\epsilon}{\epsilon + (1 - \epsilon)A}\right)(-2\pi pabc)x \int_{\xi}^{\infty} \frac{ds}{(s + a^2)^{3/2}(s + b^2)^{1/2}(s + c^2)^{1/2}} \quad \text{(A-8)}$$

where the cartesian coördinate x has been introduced in place of an equivalent expression in terms of the elliptical coördinates. The quantity A is the integral defined by eq. 6 of the main text. The integral appearing in (A-8) can be shown to approach, for large ξ, the limiting value $^2/_3r^3$, where r is the distance to the center of the ellipsoidal system, so that (A-8) shows that the potential is that of a dipole of total moment

$$m'' = \left(\frac{3}{\epsilon + 2}\right)\left(\frac{\epsilon}{\epsilon + (1 - \epsilon)A}\right)\left(\frac{4\pi abc}{3}\, p\right) \quad \text{(A-9)}$$

Since the volume of the small ellipsoid is $4\pi\ abc/3$, the last parenthesis of (A-9) is just the total moment m' of the ellipsoid of fixed polarization.

Finally, we relate the moment m'' of a macroscopic sphere, containing at its center a specified ellipsoid, to the moment m of a boundless dielectric containing the same ellipsoid. These quantities are connected by an equation first used by Kirkwood,[2] and discussed subsequently by Harris and Alder.[21] The result is

$$m = \left(\frac{\epsilon + 2}{3}\right)\left(\frac{2\epsilon + 1}{3\epsilon}\right) m'' \quad \text{(A-10)}$$

Combining (A-10) with (A-9), and introducing m' as discussed already, one may find

$$m = m' \left(\frac{2\epsilon + 1}{3}\right)\left(\frac{1}{\epsilon + A(1 - \epsilon)}\right) \quad \text{(A-11)}$$

Reviewing the definitions of m, m' and A, we see that (A-11) has the same meaning as eq. 9 of the main text.

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[20] See, for example, J. A. Stratton, "Electromagnetic Theory," McGraw-Hill Book Co., New York, N. Y., 1941, pp. 207ff.

[21] See appendix 1 of reference 3.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE U. S. NAVAL ORDNANCE TEST STATION]

The Reaction of Methyl Radicals with Deuterium

BY JAMES R. MCNESBY, ALVIN S. GORDON AND S. RUVEN SMITH

RECEIVED SEPTEMBER 12, 1955

The photolysis of acetone in the presence of deuterium has been investigated with a mercury resonance lamp and a medium pressure mercury arc with self reversed resonance line. The system has been studied from 140–450°, including the effect of surface, incident light intensity, helium and pressure. The activation energy for the abstraction of D from D_2 by a methyl radical was found to be 11.9 kcal. The experiments with 2537 Å. radiation showed greatly increased relative amounts of CH_3D formed from mercury sensitized production of D atoms, followed by a reaction taking place at least partly on the wall between CH_3 and D atoms to form CH_3D.

Introduction

The activation energy for the reaction

$$CH_3 + H_2 \longrightarrow CH_4 + H \quad (1)$$

has been the subject of some disagreement. Anderson and Taylor[1] studied the photolysis of cadmium dimethyl in the presence of H_2 and reported the activation energy for reaction (1) is 13 ± 2 kcal. Since that time Davison and Burton[2] have reported that $E_1 \approx 13$ in agreement with Anderson and Taylor, while Steacie and his co-workers[3–5] have differed sharply, and contend that $E_1 \approx 10–11$ kcal. The extent of the disagreement is illustrated in Table I, which summarizes the findings of various workers on the reactions of methyl and deutero methyl radicals with H_2 and D_2.

Davison and Burton studied the reaction

$$CH_3 + D_2 \longrightarrow CH_3D + D \quad (2)$$

by photolysis of acetone in the presence of D_2 in the temperature range 150–450°. The Arrhenius plot of the CH_4/CH_3D ratio gives two straight lines which intersect at about 350°. The slope of the 150–350° line gives an E_2 in good agreement with both Whittle and Steacie's[4] and with Marjury and Steacie's[3] values, while the slope of the 350–450° curve gives an E of 14 kcal. They accepted the higher value, suggesting that the lower value resulted from hot radical effects. They pointed out that reaction (1) has an activation energy about 1 kcal. lower than reaction (2), and therefore $E_1 \approx$

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[1] R. D. Anderson and H. A. Taylor, *J. Phys. Chem.*, **56**, 498 (1952).

[2] S. Davison and M. Burton, THIS JOURNAL, **74**, 2307 (1952).

[3] T. G. Marjury and E. W. R. Steacie, *Can. J. Chem.*, **30**, 800 (1952).

[4] E. Whittle and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 993 (1953).

[5] R. E. Rebbert and E. W. R. Steacie, *Can. J. Chem.*, **32**, 113 (1954).

TABLE I

	Anderson and Taylor.[1,a]	Davison and Burton[2,b]	Majury and Steacie[3,c]	Whittle and Steacie[4,d]	Rebbert and Steacie[1,e]	This work
(1) $CH_3 + H_2 \longrightarrow CH_4 + H$	13 ± 2	>13	9.7 ± 0.6[g,i]			
(2) $CH_3 + D_2 \longrightarrow CH_3D + D$		>14	11.6 ± 0.1[g]	11.7[g]	12.7 ± 0.5	11.9
(3) $CD_3 + H_2 \longrightarrow CD_3H + H$			10.2 ± 0.2	10.7[f]		
(4) $CD_3 + D_2 \longrightarrow CD_4 + D$			10.9 ± 0.3[f,h]			

Sources of methyl radicals: [a] Cadmium dimethyl photolysis. [b] Acetone and acetaldehyde photolysis. [c,d] Acetone and acetone-d_6 photolysis. [e] Mercury dimethyl photolysis. [f] Using E = 11.3 for $CD_3 + A_{D_6} \rightarrow CD_4 + CD_2COCD_3$. [g] Using E = 9.6 for $CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3$. [h] Obtained by measuring $CD_4/C_2D_6^{1/2}$ as function of temperature in acetone-d_6–D_2 mixture. [i] Obtained by measuring $CH_4/C_2H_6^{1/2}$ as function of temperature in acetone-H_2 mixture.

13 kcal. Wijnen and Steacie[6] criticized the work of Davison and Burton on the basis that some of their high temperature results were obtained at between 10 and 40% decomposition of acetone, and were therefore unreliable. The high temperature results of Davison and Burton at low percentage decomposition appear to be in harmony with the low temperature results of Steacie and his co-workers.

Majury and Steacie[3] studied the reaction

$$CD_3 + D_2 \longrightarrow CD_4 + D \qquad (4)$$

and reported $E_4 \approx 10.9 \pm 0.3$ kcal.

In order to decide whether hot radicals are of importance in the work of Steacie, we have reinvestigated reaction (2) from 140 to 450°.

Experimental

The photolysis apparatus has been described in a previous paper from this Laboratory.[7] Two light sources were used, a Hanovia S.C. 2537 lamp and a Hanovia S. H. Model medium pressure arc which exhibits complete reversal of the 2537 Å. resonance line and has relatively intense radiation in the 3130 region. A camera diaphragm was placed between the light source and the reaction vessel, and at all apertures the entire face of the reaction vessel was illuminated.

A reaction vessel containing enough fused silica rod to increase the surface/volume ratio by a factor of six was used in some experiments. Each furnace had a Corning 7910 filter to remove radiation in the 1849 region.

A master mixture was made up of acetone and D_2 in the ratio D_2/acetone = 1.977. All runs were made with this mixture. In addition, to the photolysis, a number of pyrolyses were carried out in the region of 500° with the above mixture, using a technique described earlier.[8] Mass spectrometer analyses were carried out on a Consolidated 21–103 instrument modified with a high resolution arrangement, so that CO and traces of air or water did not interfere with the 16 and 17 peaks of the methanes.

Results and Discussion

With a camera diaphragm inserted between the medium pressure Hg arc source and the reaction vessel at an aperture of f 4.5, 100 mm. of a mixture of acetone and D_2 in the ratio D_2/acetone = 1.977 was photolyzed at 140 and 424°. The results are given in Table II.

The methane producing reactions are

$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_2COCH_3 \qquad (5)$$

$$CH_3 + D_2 \longrightarrow CH_3D + D \qquad (2)$$

It follows that

$$CH_4/CH_3D = k_5[CH_3COCH_3]/(k_2[D_2]) \qquad 1$$

We find the activation energy difference $E_2 - E_5$ = 2.3 kcal. given by the slope of the plot of log CH_4/CH_3D *vs.* $1/T$. The value reported by Whittle and Steacie[4] over a smaller temperature range is $E_2 - E_5$ = 2.1 kcal. There appears to be no indication that high photolysis temperatures cause the CH_4/CH_3D ratio to be inconsistent with the Arrhenius plot at low temperatures. Therefore, the results of Burton and Davison at high temperatures are probably to be attributed to experimental error.

TABLE II

THE PHOTOLYSIS OF ACETONE IN THE PRESENCE OF D_2 USING A MEDIUM PRESSURE MERCURY ARC

T, °C.	*t*, min.	CH_4/CH_3D	k_H/k_D	$\frac{CH_3D \times 10^6}{D_2(t)}$	$\frac{CH_3D}{HD}$
141	6	4.68	9.25	0.56	..
141	9	4.50	8.90	0.54	..
140	20	4.29	8.48	0.56	..
140	35	4.03	7.97	0.53	..
140	50	3.85	7.61	0.62	..
424	4	1.48	2.92	31.70	1.3
424	6	1.45	2.87	32.75	1.2

The same mixture was photolyzed in a more extended study under a variety of conditions using the SC 2537 light source. The interesting results of these experiments, using a diaphragm opening of f 4.5, are shown in Table III and Fig. 1. The precipitous fall in the CH_4/CH_3D ratio at low temperatures when a 2537 Å. source was used, immediately suggested mercury sensitization as a possible cause. It is evident that CH_3D is formed by another reaction in addition to reaction (2) in the presence of mercury resonance radiation. Analysis of the product gases reveals that HD is formed in amounts far in excess of the amounts of CH_3D produced with 2537 radiation. It is to be expected that the ratio CH_3D/HD should equal unity if the only source of D atoms is

$$CH_3 + D_2 \longrightarrow CH_3D + D \qquad (2)$$

This is approximately the case when the photolysis is carried out with the medium pressure mercury arc or when the mixtures are pyrolyzed. Further, it is well known that small amounts of mercury vapor can photosensitize the production of H or D atoms from H_2 and D_2, respectively. The large amounts of HD formed and the large increase in the rate of production of CH_3D relative to CH_4 at low temperatures provide strong evidence that D atoms are involved in the production of excess CH_3D. To check the existence of Hg sensitization a mixture of approximately equal amounts of H_2 and D_2 at 28 mm. pressure and 141° was irradiated by the SC 2537 source for 15 minutes. The resulting mixture contained as much HD as D_2, proving that mercury sensitization was occurring in the system.

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(6) M. H. J. Wijnen and E. W. R. Steacie, *Disc. Faraday Soc.*, **14**, 118 (1953).

(7) J. R. McNesby and A. S. Gordon, THIS JOURNAL, **76**, 4196 (1954).

(8) J. R. McNesby, T. W. Davis and Alvin S. Gordon, *ibid.*, **76**, 934 (1954).

TABLE III

PHOTOLYSIS OF ACETONE IN PRESENCE OF D_2 WITH SC 2537 LAMP

The figures for the relative amounts of the various compounds are mass spectrometer peak heights. The D_2 peak height is included so that some idea of percentage reaction is evident. k_H is the rate constant for reaction 5 and k_D for reaction 2. The standard sensitivity for H_2 is 18.8 and for CH_4, 26.8 divisions per micron pressure. Initial pressure = 100 mm. at the temperature of the experiment. Diaphragm aperture f 4.5.

T, °C.	t, min.	CH_4	CH_3D	CH_2D_2	HD	D_2	k_H/k_D	$10^6 \times CH_4/D_2(t)$	CO/CH_4
141	5	13.1	8.9	1.6	153.0	9,010	2.91	3.03	8.42
141	15	35.7	23.0	2.4	332.0	8,220	3.06	3.02	8.64
141	20	57.8	38.2	3.6	497.0	10,000	2.99	3.01	9.79
159	7	27.7	13.7	2.0	200.4	11,980	3.99	3.44	5.50
159	14	46.8	23.2	2.4	320.0	10,200	3.99	3.41	6.33
159	21	66.1	32.9	2.6	446.0	9,650	3.97	3.40	6.82
193	7	37.8	15.7	1.6	185.7	9,000	4.76	6.25	4.35
193	15.6	81.6	34.2	1.8	345.0	8,950	4.73	6.09	4.18
220	3	25.5	12.8	1.5	147.0	10,070	3.93	8.79	3.7
220	6	41.8	19.1	1.3	180.9	8,040	4.33	9.03	3.4
220	9	66.7	30.9	1.8	263.7	8,530	4.27	9.05	3.3
258	2	20.4	10.4	1.0	84.1	7,860	3.87	13.52	2.4
258	5	65.2	32.8	1.6	186.9	8,310	3.93	16.35	2.3
258	8	97.5	46.7	1.7	240.3	7,790	4.13	16.30	2.3
303	2	42.3	23.7	1.7	...	....	3.54	...	1.9
303	4	89.8	49.1	2.1	...	....	3.62	...	1.8
303	6	147.2	79.3	2.4	...	....	3.66	...	1.7
361	1	25.6	15.5	1.3	72.4	7,580	3.26	35.18	1.1
361	2	50.9	31.0	1.4	99.0	6,870	3.24	38.59	1.3
361	4	102.6	62.8	1.9	165.3	6.700	3.22	39.88	1.3
428	1	46.0	32.5	1.9	82.1	6,460	2.81	74.18	0.7
428	2	94.1	68.3	4.4	135.9	6,480	2.73	75.63	1.0
428	3	141.0	106.8	7.6	174.9	6,210	2.61	78.83	1.2

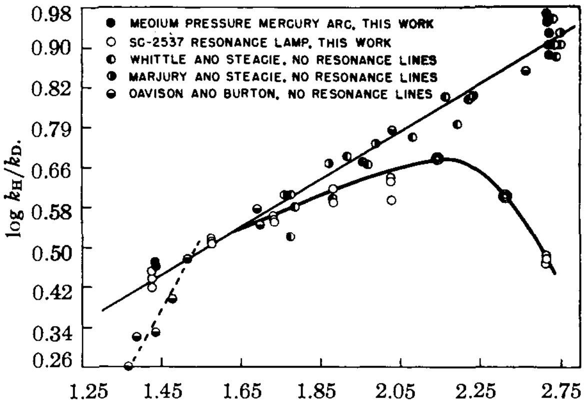

Fig. 1.

Steacie and Darwent[9] have shown that the Hg photosensitized reaction of acetone proceeds *via* the same mechanism as the unsensitized reaction. The increase in $[CH_3]$ resulting from photosensitization is unimportant to the conclusions in this work. We have confirmed the results of Steacie and Darwent on mixtures of acetone and acetone-d_6. When these mixtures are photolyzed with Hg sensitization, no H_2, HD or D_2 is produced, showing the absence of the reactions

$$Hg^* + CH_3COCH_3 \longrightarrow CH_2COCH_3 + H + Hg \quad (6)$$

$$H + CH_3COCH_3 \longrightarrow H_2 + CH_2COCH_3 \quad (7)$$

$$H + H + M \longrightarrow H_2 + M \quad (8)$$

Also the results in Table IV show that CH_4 and HD are not produced at a faster rate when the surface/volume ratio is increased. Thus these compounds are produced by homogeneous reactions.

A comparison of the results in Table III with those in Table IV shows that added surface causes the CH_4/CH_3D ratio to fall to less than one half of the ratio without added surface when a 2537 Å. source is used at low temperatures. As has been noted previously, CH_4 is not formed on the surface.

When a medium pressure lamp is used, the CH_4/CH_3D ratios do not change with fourfold pressure changes. When the light intensity was decreased to about $^1/_4$, the CH_4/CH_3D ratio was about doubled, while no significant effect on the ratio was observed when the intensity of the medium pressure source was similarly varied. Helium was added to the acetone–D_2 mixture to retard diffusion to the wall. Instead of raising the CH_4/CH_3D ratio it is lowered by about 5%. When an acetone–D_2 mixture was made up to the same total pressure as the above acetone–D_2–H_e mixture, the CH_4/CH_3D ratio was considerably raised. This complex situation may be understood if we consider the reactions of the methyl radical

$$CH_3 + D_2 \longrightarrow CH_3D + D \quad (2)$$

$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_2COCH_3 \quad (9)$$

$$D + CH_3 + M \longrightarrow CH_3D + M \quad (10)$$

$$D + CH_3 + \text{wall} \longrightarrow CH_3D + \text{wall} \quad (11)$$

Reactions (2) and (9) are the normal reactions for production of CH_3D and CH_4. In the absence of

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[9] E. W. R. Steacie and B. Darwent, *J. Chem. Phys.*, **16**, 230 (1948).

TABLE IV

EFFECT OF VARYING CONDITIONS ON APPARENT k_H/k_D

Light source	Intensity	Added surface	Total pressure, mm.	He pressure, mm.	T, °C.	t, min.	CH_4	CH_3D	k_H/k_D	CH_4/D_2t[a]	HD/D_2t[a]
SC2537	f 4.5	7x	100	..	267	2	39.6	20.1	3.89		
					267	5	77.1	36.2	4.21		
					267	8	120.7	59.1	4.03		
					431	1	45.3	30.1	2.97		
					431	2	90.6	62.7	2.85		
					431	3	142.0	102.5	2.75		
SC2537	f 4.5	..	25	..	429	3	88.6	68.4	2.57		
					429	6	173.1	133.7	2.57		
					142	10	18.6	17.6	2.10	6.1	63
					142	20	32.4	27.6	2.31	5.6	56
					142	30	52.0	41.7	2.47	5.6	53
SC2537	f 4.5	7x	25		145	7	16.8	23.9	1.38	4.9	54
					145	14	28.6	39.7	1.42	5.5	55
					145	21	42.7	58.7	1.44	5.1	50
SC2537	f 4.5	..	100	75	141	7	10.5	10.9	1.90		
					141	14	17.8	16.9	2.08		
					141	21	21.2	18.9	2.21		
SC2537	f 16	..	100	..	141	30	16.7	5.6	5.89		
					154	60	36.7	12.2	5.95		
					157	95	87.7	26.7	6.48		
					427	4	33.5	23.4	2.83		
					427	8	74.2	55.9	2.63		
					427	12	143.8	111.4	2.55		
Med. press	Full beam	..	100	..	145	20	91.3	23.4	7.71		
Med. press	f 4.5	..	25	..	141	10	5.8	1.5	7.7		
					141	20	10.0	2.6	6.5		
					141	30	13.6	2.9	9.3		
Med. press	f 4.5	..	100	75	142	10	4.4	1.1	7.9		
					142	20	7.3	1.9	7.5		
					142	30	15.5	3.2	9.5		

[a] The units are mass spectrometer divisions of CH_4 or HD per 10,000 divisions of D_2 per min.

large D atom concentrations, these are the only important reactions. Thus the CH_4/CH_3D ratio generated by the medium pressure lamp is stable to light intensity, pressure and inerts.

For the 2537 source, increase of surface increases CH_3D formation *via* reactions (10) and (11) with the result that CH_4/CH_3D ratio falls.

When a large excess of helium is introduced to retard diffusion, reaction (11) is retarded but reaction (10) increases, and the CH_3D rate actually increases about 5% over the situation in the absence of helium, thus lowering the CH_4/CH_3D ratio slightly.

If an acetone–D_2 mixture is made to the same pressure as the above mixture of acetone–D_2–He, the CH_4/CH_3D ratio is sharply increased over the ratio resulting from the He containing mixture, although this ratio is still much lower than the normal CH_4/CH_3D ratio obtained from the medium pressure lamp. This shows that reaction (11) is suppressed and that reactions (2) and (9) which are bimolecular moderate the effect of the termolecular reaction (10). It has been assumed in reactions (10) and (11) that the excess CH_3D is due to the reaction of CH_3 and D at the wall and by a three body process in the gas phase. However, three other possibilities may be examined

$$CH_3COCH_3 + D \longrightarrow CH_3D + COCH_3 \quad (12)$$

$$COCH_3 + D \longrightarrow CH_3D + CO \quad (13)$$

$$CH_3COCH_2 + D \longrightarrow CH_3D + COCH_2 \quad (14)$$

None of these reactions should require a third body in the gas phase, contrary to our observations.

The decrease in the rate of CH_3D production from CH_3 + D with increasing temperature is probably due to a decrease in the CH_3 concentration. A rough calculation of the effect of temperature *vs.* (CH_3) shows that the (CH_3) will decrease rapidly enough with increasing temperature to explain the observations.

A few pyrolysis experiments were carried out using the same mixture. The total pressure was about 250 mm. at the temperature of pyrolysis. The data are presented in Table V. The ratio CH_4/CH_3D is somewhat higher in quartz than in Pyrex. In quartz the ratio is in fairly good agreement with the extrapolation of the Arrhenius plot of the photolysis results, using the medium pressure mercury arc light source.

TABLE V

PYROLYSIS OF MASTER MIXTURE OF ACETONE AND D_2

	T, °C.	t, min.	Mass spectrometer peak heights CH_4	CH_3D	k_H/k_D
Pyrex	509	2	66.6	44.0	2.99
	509	3	94.5	64.3	2.91
	509	4	103.7	71.8	2.85
Quartz	510	2	34.5	24.9	2.75
	510	3	51.0	38.1	2.65
	510	4	60.6	46.9	2.55

Acknowledgment.—The authors wish to thank

Mr. Andreas V. Jensen and Mrs. Helen R. Young for their assistance in carrying out the mass spectrometer analyses.

CHINA LAKE, CALIF.

[CONTRIBUTION NO. 2042 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Photochemical Studies with Rigid Hydrocarbon Solvents at Low Temperatures

BY RONALD G. SOWDEN[1] AND NORMAN DAVIDSON

RECEIVED OCTOBER 7, 1955

Experiments aimed at the production of free radicals by the photolysis of suitable solutes in rigid hydrocarbon glasses at 77°K. have been performed. Acetophenone and diphenylmercury are not decomposed by irradiation in a rigid solvent at 77°K., whereas they do decompose by non-chain processes at room temperature in fluid solvents. Tetramethyltetrazene, $(CH_3)_2N—N=N—N(CH_3)_2$, is completely decomposed at 77°K., and partially reforms when the solvent melts. $(CH_3)_2N_3$ radicals may be present, but no definitive spectrum of this species was obtained. S_2Cl_2 is completely dissociated by irradiation at 77°K., and a new absorption band at 237 mμ appears. This may be due to SCl. The spectrum previously attributed to SCl_2 is probably due to S_2Cl_2. Complex effects following the irradiation of bromine, bromal and bromopicrin are described. Iodine solutions in the hydrocarbon glass used here become yellow upon cooling, but are not decolorized by irradiation.

A number of experiments aimed at the production of trapped free radicals at low temperatures have been described recently.[2,3] Of particular interest to us is the work of Norman and Porter involving visible or ultraviolet irradiation of suitable substrates in hydrocarbon or EPA glasses at the temperature of liquid nitrogen (77°K.). Using spectroscopic methods for detecting the effects of irradiation, these authors have obtained evidence for the dissociation of molecular iodine and of ethyl iodide, and for the production of CS from CS_2, ClO from ClO_2, and benzyl from a number of compounds.

To the extent that this technique is generally applicable, it will be of great value to the study of the properties of free radicals and other unstable species. The experiments reported below have been performed in order to further investigate the method. Our work has not resulted in the production and unequivocal identification of a free radical or other primary photochemical product. In two cases, it has been clearly demonstrated that the quantum yield for photo-dissociation in a rigid solvent is extremely low. In other cases, spectroscopic changes have been produced by irradiation, but definitive identification of the products was not possible. It is possible that apparently minor variations in technique will have important effects in experiments like those reported here. We believe that the accumulation of empirical experience will be helpful in the further development of this method for the study of unstable species. For this reason, our experiments are described below in considerable detail.

Materials.—Philips "Pure Grade" isopentane and 3-methylpentane were allowed to stand over sodium wire. They were then passed through activated silica gel several times, as recommended by McConnell and Tunnicliff.[4] The very slight absorption of the solvents in 1-cm. cells at 210 mμ indicated that the concentration of benzene or toluene was less than 10^{-5} *M*.

Acetophenone, diphenylmercury, bromal and bromopicrin were Eastman Kodak products. Tetramethyltetrazene was kindly supplied by Dr. H. W. Kruse of the Naval Ordnance Test Station, China Lake, California; it had been prepared as described by Renouf.[5] The sulfur monochloride was reagent grade.

Apparatus and Technique.—Spectra were recorded using a Cary model 11 M recording spectrophotometer. Figure 1 depicts the low temperature apparatus. The outer aluminum container C can be mounted snugly and reproducibly in the spectrophotometer, with quartz windows W in the light path. The steel lid L has metal ground joints for evacuation and for attachment of the Pyrex glass liquid nitrogen reservoir R. The Pyrex cell P is made with a large bore neck for ready degassing, and to avoid formation of a concave meniscus in the light path when the solution is frozen, due to thermal contraction. The path length was usually 1.5 cm. Quartz windows were cemented to Pyrex tubes with an epoxy cement.[6] These seals withstood repeated cooling to 77°K and deteriorated only very slowly in contact with hydrocarbon solvents at room temperature.

Most of the experiments were performed with a 5:1 isopentane-3-methylpentane mixture as the glass-forming solvent. Generally speaking, solute concentrations of less than 10^{-3} *M* were used, and clear glasses were obtained on cooling. Greater concentrations often resulted in formation of a semi-opaque mass on cooling, suggesting that crystallization of the solute had occurred. Glasses were formed as rapidly as possible by immersing most of the solution in liquid nitrogen, but leaving an upper portion clear to allow for the *ca.* 25% thermal contraction. Measurements with a copper-constantan thermocouple showed that, using this technique, solutions became rigid in about a minute and attained liquid nitrogen temperature in about three minutes. At about 88°K., the thermocouple wires could be moved sluggishly within the glass; at about 95°K., the mixture was quite fluid.

Irradiations were carried out with an Osram HBO 200 watt high pressure mercury arc at a fixed distance from the cell (7.5 cm.) with no lenses. Tests with a thermocouple frozen in just above the light path showed that irradiation of a pure hydrocarbon glass resulted in no warmup provided the reservoir was full of liquid nitrogen. If the nitrogen was just above the light path, there was a steady state warmup of 6°. This could be decreased by using water as an infrared filter. While recording spectra, liquid nitrogen could be removed from the light path. Thermocouple measurements showed that, provided some liquid nitrogen remained in contact with the bottom of the cell, there was no warmup. An approximate estimation of the light output of the arc was obtained. A sample of HBr gas at a pressure

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