

ence observed at low temperatures could be due to a heterogeneous decomposition of the ester on the wall. A more systematic investigation of the pyrolysis at low temperatures will be undertaken in the near future.

It has been suggested¹¹ that a photochemically induced rearrangement may be considered to be an

(11) J. Franck and H. Sponer, "Volume Commemorative V. Henri," Editions Desoer, Liège, Belgium, 1947, p. 169.

internal conversion involving a transition from one electronic state to a high level of vibration of a lower electronic state, thus producing a vibrationally excited molecule which may be expected to behave like a normal, thermally activated molecule. A comparison of the data from photolysis with those from pyrolysis indicates that there is no obvious analogy between the two modes of decomposition.

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.]

The Effect of Solvents on the γ -Ray Radiolysis of Methyl Acetate and Acetone

By P. J. AUSLOOS

RECEIVED AUGUST 22, 1960

The effect of cyclohexane and benzene on the radiolysis of $\text{CH}_3\text{COOCH}_3$, $\text{CH}_3\text{COOCD}_3$, and mixtures of $\text{CH}_3\text{COCH}_2\text{-CD}_2\text{COCD}_3$ has been investigated at 17° . In the absence of scavengers, cyclohexane markedly reduces the yield of CO, whereas, in the presence of scavengers, it produces no effect. Benzene inhibits the decomposition of methyl acetate and acetone. Hydrogen is mostly formed in processes involving "hot" hydrogen atoms. The effect of the solvents on the yields of ethanes and some of the methanes indicates the importance of cage and intercage recombinations and disproportionations of the radicals in the γ -ray track. The radiolysis of a $\text{CH}_3\text{COCH}_2\text{-CD}_2\text{COCD}_3$ mixture at -195° is discussed briefly.

Introduction

The liquid-phase radiolysis of acetone¹ and methyl acetate^{2,3} has been investigated recently. The present paper reports the results of studies of the effect on the radiolytic decomposition of these compounds of varied amounts of benzene and cyclohexane. The studies were designed to reveal more detailed information on: (a) the reactions occurring in the γ -ray track, (b) the formation of the hydrogen molecule and (c) the scavenging action of carbon monoxide.

Experimental

Materials.—The compounds $\text{CH}_3\text{COOCD}_3$ and $\text{CD}_2\text{-COCD}_3$ were obtained from Merck and Company. They were purified by a trap-to-trap distillation at -80° and, subsequently, by distillation into the storage bulb from a trap at -40° . Mass-spectrometric analysis showed that the per cent. of deuterium in the deuterated acetone was 99.5 atom % of D and the methyl acetate to be 98.6% $\text{C}_2\text{H}_5\text{D}_2\text{O}_2$. From the cracking pattern, it was deduced that only the methoxy group was fully deuterated.

"Spectrograde" CH_3COCH_3 , C_6H_6 and C_6H_{12} were obtained from Eastman Kodak Company and used without further purification. All compounds were thoroughly degassed.

2,2-Diphenyl-1-picrylhydrazyl (DPPH) was obtained from Aldrich Chemical Company and was kept under vacuum until it was introduced into the cell.

Irradiations.—The liquids were irradiated in sample tubes made of Pyrex tubing, which were 15 cm. long and had an internal diameter of 0.35 to 0.8 cm. Each cell was provided with two outlets; one was sealed after filling and the other was closed by a break seal. The cells were filled by expanding each compound from its storage bulb into a one-liter bulb provided with a mercury manometer. After recording the pressure, the material was condensed into the reaction cell at -80° . The amount of methyl acetate or acetone introduced into the sample tube was 1 cc. and different amounts of cyclohexane or benzene subsequently were condensed into the cell. The diameter of the cell was adjusted in such a way that the liquid level was constant to within 3 mm. This procedure was adopted in order to insure a constant dose rate and to keep the methyl acetate or acetone conversion approximately constant without greatly

affecting the amount of products formed. The 2000-Curie source at the National Bureau of Standards was used in this investigation. It consists of twelve cobalt-60 sticks (19 cm. high, 1 cm. thick) arranged in a circular pattern (9 cm. i.d.) at the bottom of a water pool.

Usually, six samples were arranged in a reproducible, symmetrical pattern inside a cylindrical metal container. The container was sealed and then lowered into the center of the pool. The experiment at -195° was performed by immersing the sample in a narrow Dewar flask containing liquid nitrogen and placing the Dewar in the container.

The rates of absorption of energy were determined from the concentrations of ferric ion formed by irradiating 1 cc. of ferrous sulfate solutions. Assuming that $G(\text{Fe}^{+++}) = 15.45$, the rate of energy absorption was calculated to be 4×10^{17} ev./cc./min. In order to make the discussion easier to follow, the data given in Tables I, II and III are expressed in molecules/cc./min. multiplied by the ratio $(V_A + V_S)/V_A$. In this ratio, V_A is the volume of methyl acetate or acetone, and V_S is the volume of solvent. Both volumes are measured at STP. If required, the G values can easily be calculated from the dose rate given above.

TABLE I
RADIOLYSIS OF CYCLOHEXANE- $\text{CH}_3\text{COOCH}_3$ MIXTURES AT 17°

Concn. cyclohexane, mole %	Concn. scavenger, $10^{-3} M$	Time, min.	Rate $\times (V_A + V_S)/V_A \times 10^{-14}$, molec./cc./min.			
			H ₂	CH ₄	C ₂ H ₆	CO
..	..	110	3.37	7.38	1.75	6.82
..	..	365	3.83	7.42	1.58	5.83
..	I ₂	110	2.67	2.73	1.14	6.82
16.2	..	365	7.80	7.95	1.47	4.54
31.0	..	365	13.40	9.05	1.66	2.38
31.0	..	110	12.50	9.15	1.65	4.75
31.0	I ₂	360	8.00	2.85	0.95	6.75
46.0	..	110	16.80	9.75	1.62	3.80

Analysis.—The analytical procedure was essentially the same as that described previously.^{1,3} Hydrogen, methane and carbon monoxide were distilled out at -195° , the C_2 fraction at -175° and the CO_2 fraction at -150° . All three fractions were analyzed with the mass spectrometer. Reference samples of CH_3CD_3 and C_2D_6 (obtained from Merck and Company) were analyzed in order to obtain reliable cracking patterns. The distribution of the methanes was calculated from cracking patterns reported in the literature.⁴

(1) P. Ausloos and J. Paulson, *THIS JOURNAL*, **80**, 5117 (1958).

(2) P. Ausloos and C. M. Trumbore, *ibid.*, **81**, 3866 (1959).

(3) R. W. Hummel, *Trans. Faraday Soc.*, **56**, 234 (1960).

(4) F. L. Mohler, V. H. Dibeler and E. Quinn, *J. Research Natl. Bureau Standards*, **61**, 171 (1958).

TABLE II
 RADIOLYSIS OF BENZENE-CH₃COOCD₃ MIXTURES DURING 150 MIN. AT 17°

C ₆ H ₆ mole %	..	5.4	13.6	30.0	52.0	52.0	68.5	77.0	
I ₂ 10 ⁻³ M	Yes	Yes	
Rate × (V _A + V _S)/V _A × 10 ⁻¹⁵ molec./cc./min.									
H ₂	0.72	0.56	0.615	0.608	0.628	0.712	0.64	0.805	1.01
HD	.70	.585	.525	.475	.404	.326	.28	.247	0.238
D ₂	.43	.493	.326	.278	.207	.156	.14	.112	0.106
CO	5.32	5.30	4.87	4.52	4.26	4.13	4.00	3.72	3.76
CO ₂	3.45	3.46	3.30	..	3.04	2.65	..	2.37	2.38
Ethane	0.97	0.826	0.817	0.703	0.610	0.475	0.393	0.46	0.458
CH ₄ /CO	.61	.037	.57	.59	.578	.545	.041	.55	.548
CH ₃ D/CO	.24	.192	.22	.20	.174	.162	.116	.148	.148
CD ₃ H/CO	.217	.024	.22	.22	.21	.198	.029	.210	.204
CD ₄ /CO	.058	.050	.048	.04	.03	.02	.014	.014	.011
C ₂ H ₆ /CO	.06	.0475	.054	.047	.043	.0288	.0207	.0226	.019
CH ₂ CD ₂ /CO	.110	.100	.108	.102	.095	.0833	.076	.0805	.082
C ₂ D ₆ /CO	.0068	.006	.0061	.0058	.0050	.0035	.00265	.00215	.00181

 TABLE III
 RADIOLYSIS OF CH₃COCH₃-CD₂COCD₃ (1:1) MIXTURES IN PRESENCE OF SOLVENTS

Solvent	C ₆ H ₁₂	C ₆ H ₁₂	C ₆ H ₁₂	C ₆ H ₆	C ₆ H ₆	C ₆ H ₆
Mole %	55	70	70	30.6	54.5	75
Scavenger	..	DPPH	DPPH
Concentration	..	1 × 10 ⁻³ M	1 × 10 ⁻³ M
Temperature, °	17	17	-195	17	17	17	17	17	17
Time, min.	100	100	100	365	150	150	150	150	150
Rates, × (V _A /V _S)/V _A × 10 ⁻¹⁵ molec./cc./min.									
H ₂	1.46	0.80	0.675	15.2	36.0	27.2	0.955	0.81	0.53
HD	0.78	.54	.385	1.8	2.28	1.83	.400	.235	.093
D ₂	0.305	.26	.150	0.15	0.122	0.107	.165	.081	.0296
CO	2.20	2.45	.275	1.10	1.44	2.05	1.92	1.51	.78
CH ₄	3.81	0.425	.770	4.08	3.50	0.67	2.00	1.44	.655
CH ₃ D	0.495	.189	.195	0.305	0.240	.085	0.266	0.128	.073
CD ₃ H	3.15	.277	.320	3.40	2.60	.42	1.32	.89	.382
CD ₄	0.488	.202	.190	0.305	0.20	.095	0.22	.135	.055
C ₂ H ₆	.82	.81	.84	.8359	.425	.32
CH ₂ CD ₂	.342	.33	.065	.203126	.065	.0385
C ₂ D ₆	.277	.275	.295	.280206	.150	.131

Discussion

A. Cyclohexane-CH₃COOCD₃ Mixtures.—It may be seen from the results for the first two experiments, Table I, that, for undiluted methyl acetate, an increase in dose by a factor of 3.3 has little effect on the yields of the measured products. These results are in agreement with those reported previously.^{2,3} There may, however, be a small decrease in the yield of CO. A leveling off of this yield as a function of dose also has been observed by Hummel.⁵

The addition of cyclohexane in the absence of scavengers leads to a pronounced reduction in the yield of CO. The facts that (a) the yield of CO decreased with an increase in dose (compare experiments 5 and 6 of Table I) and (b) the yield of CO for small doses is the same in the presence of I₂ as for the undiluted mixture indicate that these observations cannot be explained by an energy-transfer process but can be understood in terms of a reaction involving CO and a radical produced in the radiolytic decomposition of cyclohexane. The most likely reaction under these conditions is



(5) R. W. Hummel, United Kingdom Atomic Energy Authority Research Group Report AERE-R2910.

where R is either a H atom or a cyclohexyl radical.

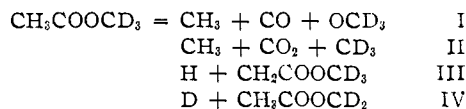
Although H atoms react with CO at a greater rate than do cyclohexyl radicals, it must be realized that the steady-state concentration of these radicals will be much greater than that of the H atoms. Hydrogen atoms undergo a fast abstraction reaction to produce H₂, especially if the H atoms are produced with excess kinetic energy. The reduction of the yield of CO observed in the case of the undiluted methyl acetate probably can be explained by reaction 1, where R is one of the radicals produced, either in the primary split or in any subsequent reaction. It may be pointed out that reactions similar to (1) have been assumed to occur in the liquid phase.⁶ The effect of cyclohexane on the yields of methane and ethane are rather minor, both in the presence or absence of I₂.

B. Benzene-CH₃COOCD₃ Mixtures.—The addition of benzene leads to a reduction in the yields of all measured products (except H₂). In this case, it would be difficult to explain the decrease in the yield of CO by reaction (1) because the yield of radicals in the radiolytic decomposition

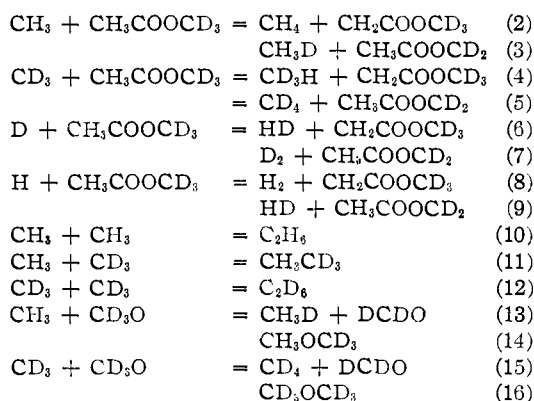
(6) (a) D. D. Coffman, R. Cramer and W. E. Mochel, THIS JOURNAL, **80**, 1881 (1958); (b) C. Walling and E. S. Savas, *ibid.*, **82**, 1738 (1960).

of benzene is known to be small.⁷ A more likely explanation for this decrease would invoke an energy-transfer process involving the benzene molecule. The results in Table II are in agreement with this explanation, since they indicate that, in contrast with the cyclohexane-methyl acetate mixtures discussed before, the yield of CO is not significantly different in the presence of radical scavengers. The fact that the ratio CO/CO₂ is essentially independent of the benzene concentration gives additional support to the view that benzene inhibits the decomposition of methyl acetate. The fact that the yields of HD and D₂ are diminished much more than that of CO can be attributed to the scavenging action of benzene for radicals. It should be pointed out that, in a recent investigation⁸ of the radiolysis of methyl acetate-benzene mixtures, an inhibition in the decomposition of the methyl acetate by benzene in the presence of DPPH was not observed, when the experiments were done under vacuum. However, in the presence of oxygen, inhibition was observed at low concentrations of benzene.

In a previous study on the radiolysis of CH₃-COOCD₃,³ the over-all primary dissociations suggested were



It is understood that processes I and II may also be written as a sequence of two steps involving the intermediate species: CH₃CO, CH₃CO₂, CO₂-CD₃, and that radicals CH₂COOCD₃ and CH₂-COOCD₂ may dissociate into smaller fragments. These secondary reactions were proposed for explaining the products



Although it was shown that CH₄ and CD₃H are produced almost exclusively by abstraction reaction 2 and 4, it was also shown that CH₃D and CD₄ could only be accounted for by assuming that they were mostly formed in the disproportionation reactions 13 and 15 in the γ -ray track. The fact that, in the presence of scavengers, CD₄, as well as C₂H₆ and C₂D₆, is produced, is evidence that radicals originating from different parent molecules do recombine and disproportionate in the track

(7) A. Prevost-Bernas, A. Chapiro, C. Cousin, Y. Landler and M. Magat, *Discussions Faraday Soc.*, **12**, 98 (1952).

(8) L. Bouby and A. Chapiro, *J. Chem. Phys.*, **54**, 341 (1957)

(intercage effect). On the other hand, the large values of the ratios CH₃CD₃/(C₂H₆ × C₂D₆)^{1/2} and CH₃D/CD₄, as well as the changes in these ratios with temperature, were considered to be evidence that recombinations and disproportionations between radicals originating from the same molecule do occur (cage effect). If this interpretation is correct, it may be expected that dilution with solvents will greatly reduce the yields of CD₄, C₂H₆ and C₂D₆. The yields of CH₃D and CH₃CD₃ will only be reduced if the compounds are produced from radicals originating from different molecules.

Assuming that the amounts of CO and CO₂ are measures of the number of methyl and methoxy radicals initially produced, all data obtained here can be related to the yields of CO or CO₂.

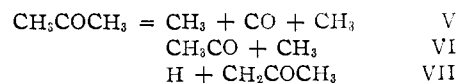
From the results given in Table II, it may be seen that, for a mixture containing 77 mole % of benzene, the ratios CH₃CD₃/CO and CH₃D/CO are diminished by not more than 40 %, both in the absence or in the presence of a scavenger. On the other hand, the ratios CD₄/CO, C₂H₆/CO and C₂D₆/CO are diminished by a factor of three or greater. The largest diminutions occur for mixtures containing more than 30 mole % of benzene.

$$\text{C}_2\text{H}_6^{1/2}/\text{C}_2\text{D}_6^{1/2} = \text{CH}_4/\text{CD}_3\text{H} = (\text{CO} + \text{CO}_2)/\text{CO}_2$$

It has been pointed out before³ that the measured ratios of yields are good evidence in favor of an equilibrium distribution of the methyl radicals in the γ -ray track if the contribution from the cage is not considered. Assuming an equilibrium distribution of the CH₃ and CD₃, the diminution of the ratio CH₃CD₃/CO with dilution can be calculated from the equilibrium equation: CH₃CD₃ = 2(C₂H₆ × C₂D₆)^{1/2}. Taking values of C₂H₆/CO and C₂D₆/CO for the experiments with undiluted methyl acetate and with 77 mole % of benzene, a reduction of CH₃CD₃/CO from 0.110 to 0.0816 can be calculated. This is in good agreement with the observed decrease and indicates once again that the methyl radicals which undergo intercage recombination are in equilibrium in the track. It may be concluded that the CH₃CD₃ and CH₃D remaining at high dilution are almost exclusively formed by recombination and disproportionation between original partners.

Benzene reduces the ratios HD/CO appreciably. This decrease can be explained as being a result of the addition to D and H atoms to benzene. The increase in the yield of hydrogen is obviously caused by the formation of H₂ in the radiolytic decomposition of benzene. A more detailed discussion of the effect of solvents on the production of HD and D₂ will be given later in this paper.

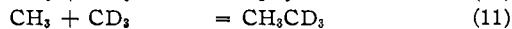
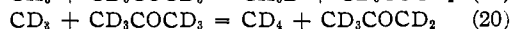
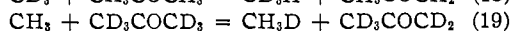
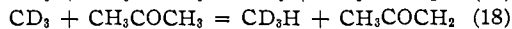
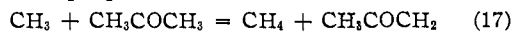
C. The Effect of Solvents on the Radiolysis of CH₃COCD₃-CD₃COCD₃ (1:1) Mixtures.—In an earlier investigation¹ of the radiolysis of acetone, the processes suggested were



It was found that $G(\text{CO})$ is independent of temperature from -80 to +27°. This fact clearly indicates that, under these conditions, CO is not formed in a thermal decomposition of the acetyl

radical and the yield of CO can be taken as a measure of the importance of step V.

For mixtures of CH_3COCD_3 and CD_3COCD_3 , the methyl radicals may undergo reactions similar to the ones proposed for $\text{CH}_3\text{COOCD}_3$



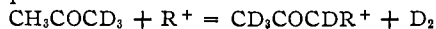
Disproportionation reactions between methyl radicals and acetyl radicals may be expected to occur as well—although to a rather minor extent, in view of the very low rate of these reactions in comparison with the recombination process producing acetone. Consequently, the methanes formed in the presence of scavengers probably come from “hot” methyl radicals reacting with acetone or from ion-molecule reaction. The near equality of the methanes produced in the presence of DPPH or iodine³ favors this interpretation.

1. Addition of Cyclohexane.—The results of Table III indicate that dilution of the acetones with cyclohexane leads to a reduction in the yield of CO. This effect is more pronounced at large dose and does not occur in the presence of scavengers. Reaction 1, proposed in Section A, appears to fit these observations.

The increase in the ratios $\text{CH}_4/\text{CH}_3\text{D}$, $\text{CD}_3\text{H}/\text{CD}_4$ and HD/D_2 with an increase in dilution is caused by methyl radicals and hydrogen atoms abstracting from cyclohexane. It is interesting to note that these trends also occur when DPPH has been added to the sample. After subtracting the methanes produced in the presence of DPPH from the methanes produced in the absence of scavengers, the ratios $\text{CD}_3\text{H}/\text{CD}_4$ and $\text{CH}_4/\text{CH}_3\text{D}$ equal approximately 11 for the undiluted mixtures and about 20 for the mixtures containing 70 mole % of cyclohexane. The latter figure is rather low, since the rate of abstraction from cyclohexane is greater than from acetone (as determined in vapor-phase studies).⁹

The fact that scavengers diminish only slightly the yield of the hydrogen molecules indicates that “hot” hydrogen atoms may be largely responsible for formation of the hydrogen molecules. The considerable reduction in the amount of D_2 and the concurrent increase in the yield of HD ¹⁰ in the presence of cyclohexane are consistent with the view that hydrogen is formed as a result of a process involving an abstraction of a hydrogen atom.

These observations are evidence against the occurrence of processes, involving the removal of a hydrogen molecule, known to occur in the vapor phase



or



(9) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

(10) The increase of HD can be ascribed to (a) H atoms originating from the radiolytic decomposition of cyclohexane which may abstract a D atom from CD_3COCD_3 and (b) D atoms abstracting H atoms from cyclohexane.

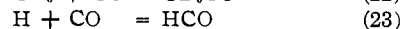
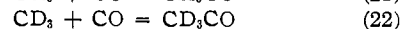
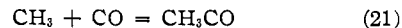
The pronounced decrease in the ratio D_2/CO for the radiolysis of the mixtures $\text{CH}_3\text{COOCD}_3$ -benzene and CH_3COCH_3 - CD_3COCD_3 -benzene supports this conclusion. In the vapor phase, however, definite evidence has been obtained for the removal of a hydrogen molecule from one carbon atom.³ It should also be noted that no evidence has been found for processes involving “hot” hydrogen atoms in the radiolysis of gaseous methyl acetate,³ in contrast with the evidence found for the occurrence of these processes in the radiolysis of the liquid.

2. Addition of Benzene.—From the decrease in the yield of CO, it may be concluded that benzene has a pronounced inhibiting effect on the radiolytic decomposition of acetone. The ratios $\text{CH}_4/\text{CH}_3\text{D}$ and $\text{CD}_3\text{H}/\text{CD}_4$ vary only slightly over the whole concentration range. The slight increase of both ratios with an increase in dilution can be explained in terms of a relatively slow abstraction of H atoms from benzene. It can also be seen that, although there is a considerable diminution of the ratios HD/CO and D_2/CO , the ratio HD/D_2 increases only slightly. These results show that benzene is mainly a scavenger for hydrogen atoms and that “hot” hydrogen atoms tend to add to benzene rather than to abstract a hydrogen atom.

3. Track Effects.—It has been pointed out that, in the radiolysis of acetone and methyl acetate, methyl radicals may recombine in the γ -ray track and that this recombination may take place either between two radicals originating from the same acetone molecule or between radicals originating from different, neighboring molecules.

In the case of mixture CH_3COCD_3 - CD_3COCD_3 , it may then be expected that solvents will diminish the ratios $\text{CH}_3\text{CD}_3/\text{C}_2\text{D}_6$ and $\text{CH}_3\text{CD}_3/\text{C}_2\text{H}_6$. It may be seen from the results given in Table III that both cyclohexane and benzene diminish these ratios considerably. The fact that benzene seems to be more effective than cyclohexane may be explained on the basis of the action of benzene in diminishing the concentration of radical in the track and hence enhancing the importance of diffusion out of the track.

D. Radiolysis of Acetone at -195° .—It may be seen from the experiment at 17° in which DPPH was added, that the distribution of the methanes is approximately the same as for the experiment on the solid phase at -195° , in which scavengers were absent. These results indicate that, at -195° , the thermalized methyl radicals either are being scavenged or are not produced. The first possibility is the more likely, in view of the very low yield of CO. The fact that $\text{CO} < (\text{C}_2\text{H}_6 + \text{C}_2\text{D}_6)$ clearly indicates that CO must have been produced initially and that, under these conditions, it acts as a scavenger. In view of the low yield of hydrogen and methane, reactions 21–24 are suggested



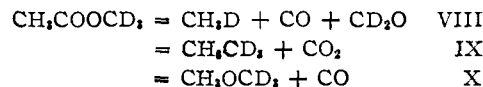
These reactions must have a low activation energy and may be expected to compete efficiently with

reactions 17-20, whose rate is considerably decreased at these low temperatures.

At -195° , the yield of CH_3CD_3 was lower by a factor of 5 than at 17° , whereas those of C_2H_6 and C_2D_6 underwent little change, clearly showing that intermolecular recombination is almost completely inhibited under these conditions.

In conclusion, it should be pointed out that the evidence for cage recombination presented in this paper and in previous studies is based solely on the following experimental results: (1) the yields of certain products, after correcting for changes in decomposition and intermolecular contributions, are independent of temperature, the presence of scavengers and of solvents, and (2) the negligible yields of these products in the vapor-phase radiolysis performed in the presence of scavengers. Because of (2), it is difficult to accept an intramolecular

rearrangement as an alternative explanation. It remains true, nevertheless, that for such a compound as $\text{CH}_3\text{COOCD}_3$, three intramolecular processes are consistent with (1)



From the mass-spectra cracking-pattern of $\text{CH}_3\text{-COOCD}_3$, it may be deduced¹¹ that the positively ionized methyl acetate molecule does not undergo any of the processes VIII to X. Also, from photochemical studies¹² on the vapor phase, no evidence has been found for the occurrence of any of these processes.

(11) A. B. King and F. A. Long, *J. Chem. Phys.*, **29**, 374 (1958).

(12) M. H. J. Wijnen, *ibid.*, **28**, 939 (1958).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

Microwave Absorption and Molecular Structure in Liquids. XXXVIII. The Effect of Structural Factors upon Group Rotation in Some Aromatic Molecules^{1,2}

BY WILLIAM P. PURCELL³ AND CHARLES P. SMYTH

RECEIVED AUGUST 29, 1960

The dielectric constants and losses at wave lengths of 1.2, 3.2, 10, 25 and 50 cm. and 575 m. have been measured for 4,4'-bis-(dimethylamino)-benzophenone in benzene solution at 20, 40 and 60° , and for 2,4,6-trinitroanisole, 2-amino-4-methylpyridine and *N,N*-dimethyl-*p*-nitroaniline in benzene solution at 20° . The data have been used to calculate the dielectric relaxation times of the molecules. The relaxation times give no positive evidence of intramolecular group rotation in these molecules, but the considerable differences indicated between the infinite-frequency dielectric constants and the squares of the refractive indices show high-frequency absorption due to such oscillational or rotational motion. The moment value 4.99×10^{-18} is found for 4,4'-bis-(dimethylamino)-benzophenone.

If a molecule has a rotatable polar group whose moment component does not lie in the axis of group rotation, the molecule can relax by group and overall molecular dipole orientations. The former mechanism has its position of maximum absorption at higher frequencies than the latter mechanism. Experimentally one observes an absorption curve which is resolvable⁴ into two peaks corresponding to the two mechanisms, or else the absorption curves are too close to one another to afford resolution, in which case one simply observes an apparent lowering of the relaxation time to be expected if the molecule were rigid. The contribution of group rotation is evident in the low relaxation times of 1,4-dimethoxybenzene, benzidine and *N,N,N',N'*-tetramethyl benzidine, which are 6.9,⁵ 1.6⁶ and 2.2×10^{-12} sec.,⁶ respectively, measured in benzene solution at 20° . These values may be compared with the relaxation time of the much smaller molecule, chlorobenzene, for which $\tau = 8.3 \times 10^{-12}$ sec.⁷ measured at 20° in benzene solution. In the present paper the authors have investigated molecules

containing methoxy, amino and dimethylamino groups with the hope of determining what influence, if any, the group has upon the dielectric relaxation and how the rotation of the group may be hindered or prevented by structural factors.

Experimental Methods

Apparatus.—The apparatus and the various methods of measurement have been described in previous papers.⁸⁻¹⁰

Purification of Materials.—4,4'-Bis-(dimethylamino)-benzophenone, obtained from Eastman Kodak Co., was recrystallized twice from ethanol and dried under vacuum in an Abderhalden pistol.

2,4,6-Trinitroanisole, obtained from Eastman Kodak Co., was recrystallized three times from ethanol and dried under vacuum in an Abderhalden pistol, m.p. $67.8-68.5^{\circ}$.

2-Amino-4-methylpyridine, obtained from Eastman Kodak Co., was recrystallized four times from ethanol and dried under vacuum in an Abderhalden pistol, m.p. $99.2-99.8^{\circ}$.

N,N-Dimethyl-*p*-nitroaniline, obtained from Matheson Coleman and Bell, was recrystallized twice from ethanol and dried under vacuum in an Abderhalden pistol, m.p. $164.5-165.2^{\circ}$.

Benzene, obtained from Allied Chemical Corp., was used without further purification.

Experimental Results

The experimental results were treated in the manner previously described.¹¹ The slopes of the

(8) H. L. Laquer and C. P. Smyth, *THIS JOURNAL*, **70**, 4097 (1948).

(9) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3443 (1950).

(10) D. A. Pitt and C. P. Smyth, *J. Phys. Chem.*, **63**, 582 (1959).

(11) A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *THIS JOURNAL*, **72**, 3447 (1950).

(1) This research was supported by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This paper represents part of the work submitted by W. P. Purcell to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(4) W. P. Purcell and C. P. Smyth, *THIS JOURNAL*, **83**, 1063 (1961).

(5) E. Fischer, *Z. Naturforsch.*, **9a**, 909 (1954).

(6) E. L. Grubb and C. P. Smyth, unpublished results.

(7) D. H. Whiffen, *Trans. Faraday Soc.*, **46**, 130 (1950).