layer structure (*not* due to concentration polarization) can be neglected; the k^0's are rate constants at some reference potential, for instance at $E = 0$ volt *versus* the normal hydrogen electrode; and the z's are the valences of O and R.

At the equilibrium potential, $E = E_e$, $i = 0$ and there is no concentration polarization. Hence, $C_O = C^0_O$ and $C_R = C^0_R$, where the C^0's are the bulk concentrations. By noting that $C^0_O/C^0_R = \exp\,[(nF/RT)(E_e - E_0)]$, where E_0 is the formal potential for O + n e = R, one can write the quantity

$$nFC^0_Ok^0_f \exp\left[-\frac{\alpha nFE_e}{RT}\right] \exp\left[\frac{(\alpha n - z_O)F(\phi_H - \phi_S)}{RT}\right]$$

in the form

$$i_O = nFC^0_O{}^{(1-\alpha)}C^0_R{}^{\alpha}k_s \exp\left[\frac{(\alpha n - z_O)F(\phi_H - \phi_S)}{RT}\right] \tag{11}$$

with k_s, the rate constant at the formal potential E^0, given by

$$k_s = k^0_f \exp\,(\alpha nFE^0/RT) = k_b{}^0 \exp\,[(1 - \alpha)nFE^0/RT] \tag{12}$$

The exchange current density i_0 can also be written in terms of only C^0_O or C^0_R by noting that $C^0_O/C^0_R = \exp\,[(nF/RT)(E_e - E^0)]$.

The current-potential characteristic

$$i = i_0 \left\{\frac{C_O}{C^0_O} \exp\left[-\frac{\alpha nF(E - E_e)}{RT}\right] - \frac{C_R}{C^0_R} \exp\left[\frac{(1 - \alpha)nF(E - E_e)}{RT}\right]\right\} \tag{13}$$

has the same form as the one previously given except that the exchange current density i_0 now depends on the double layer structure because of the term in $(\phi_H - \phi_S)$. This term would probably account for the salt effect in the absence of specific adsorption. Values of k_s should be corrected accordingly.

TABLE I

COMPARISON OF EXPERIMENTAL AND CALCULATED SHIFTS ΔE FOR REDUCTION OF 5×10^{-3} M IODATE IN 2×10^{-2} M HYDROXIDE WITH VARYING AMOUNT OF ELECTROLYTE AT 30°

C_{salt}, mole l.$^{-1}$	$E_{exp.}$ v. *vs.* S.C.E.	ΔE_{exp}, v.	$\Delta E_{calcd.}$, rigorous, v.	$\Delta E_{calcd.}$, approximate (eq. 7), v.
	$KIO_3 + KOH + KCl$[a]			
0.00	−1.173	...	...	...
.02	−1.149	0.022	0.030	0.034
.04	−1.135	.039	.047	.055
.06	−1.119	.054	.060	.071
.10	−1.104	.069	.078	.094
.25	−1.073	.102	.111	.140
.50	−1.039	.136	.133	.177
	$LiIO_3 + LiOH + LiCl$[b]			
0.00	−1.151	...	...	...
.02	−1.125	0.026	0.025	0.034
.04	−1.109	.042	.042	.055
.06	−1.097	.054	.054	.071
.10	−1.079	.072	.071	.094
.25	−1.037	.114	.103	.140
.50	−1.004	.147	.127	.177
	$KIO_3 + KOH + K_2SO_4$[c]			
0.00	−1.157	...	...	...
.02	−1.127	0.030	0.047	0.056
.04	−1.101	.056	.072	.084
.06	−1.087	.070	.087	.103
.10	−1.070	.087	.102	.122
.25	−1.042	.115	.142	.175
.50	−1.018	.139	.169	.214

[a] At 40 microamp. cm.$^{-2}$. [b] At 27 microamp. cm.$^{-2}$. [c] Same as b.

BATON ROUGE, LOUISIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

Radiolysis of Simple Ketones[1]

BY P. AUSLOOS AND J. F. PAULSON

RECEIVED MARCH 24, 1958

The liquid and vapor phase radiolysis of acetone, methyl ethyl ketone and diethyl ketone has been investigated briefly. The effect of temperature and scavengers on the G-values of the volatile products has been interpreted on the basis of known radical processes. In the case of acetone it has been shown that at least 85% of the methyl radicals are thermalized before abstracting a hydrogen atom from acetone. In the liquid phase recombination products were found to be present in appreciable amounts and were not removed by iodine or DPPH at concentrations up to 2.5×10^{-2} mole/l.

This investigation was undertaken in connection with recent studies on the liquid phase photolysis of simple ketones.[2,3] Although the photolysis results are of some help in interpreting certain features of the radiolysis studies, it is obvious that they do not contribute to the explanation of phenomena related to ion processes and track effects.

In this work only the volatile products were determined quantitatively and no attempt has been made to interpret certain minor products such as C_2H_2, C_3H_4, C_3H_6, . . ., which were formed in the vapor and liquid phase radiolyses of the ketones and which have also been detected in the radiolyses of alcohols,[4] ethers[5] and esters.[6] It may be expected that small fractions of the major products are formed by processes analogous to those responsible for these unexplained products.

Experimental

Irradiation.—The liquids were irradiated in 10 cc. Pyrex volumetric flasks with flat bottoms. In all experiments 2

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[1] This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18 (600)1528, and in part by the Atomic Energy Commission. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] R. Pieck and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1304 (1955)

[3] P. Ausloos, *ibid.*, **36**, 400 (1958).

[4] W. R. McDonnell and A. S. Newton, THIS JOURNAL, **76**, 4651 (1954).

[5] A. S. Newton, *J. Phys. Chem.*, **61**, 1485 (1957).

[6] (a) A. S. Newton and P. O. Strom, *ibid.*, **62**, 24 (1958); (b) P. Ausloos, to be published.

TABLE I

LIQUID PHASE RADIOLYSIS OF ACETONE

				G (molecules/100 e.v.)						
	Scavenger	T, °C.	Time, min.	CO	Ethane	Hydrogen	CH_4	CD_4	CH_3D	CD_3H
$CH_3COCH_3 + CD_3COCD_3$ 1:1		27	877	0.675	0.400	0.57	1.06	0.128	0.135	0.865
	2×10^{-2} M (DPPH)	27	313	.62	.378	.44	0.083	0.066	0.068	0.078
CD_3COCD_3		27	877	.64	.380	.415		2.34		
CH_3COCH_3		−80	352	.71	.512	.76	2.40			
		−80	240	.725	.525	.77	2.40			
		27	593	.835	.48	.88	2.62			
		27	650	.82	.475	.86	2.55			
		58	604	1.38	.725	1.08	3.24			
	2.5×10^{-2} M (DPPH)	58	260	0.83	.395	0.75	0.42			
	2.5×10^{-2} M (DPPH)	27	264	.71	.363	.67	.345			
	2.0×10^{-2} M (I_2)	27	593	.70	.361	.66	.33			

cc. of liquid, measured at NTP, was distilled into the irradiation cell after thorough degassing of the sample. The cell was provided with two outlets, one of which was sealed after filling, while the other was closed by a break seal. The cell was always put in the same position with respect to the cobalt source. Radiation entered through the bottom of the cell. Low temperature experiments were performed by bringing the cell into contact with Dry Ice. For runs done at temperatures above room temperature the cell was surrounded by an electrically heated jacket.

Determination of the ferric ion concentration produced by irradiating 2 cc. of ferrous sulfate solutions, and taking $G(Fe^{+++}) = 15.45$,[7] led to a value for the absorbed intensity of 2.17×10^{17} e.v./cc. min. All results have been expressed in number of molecules produced per 100 e.v., assuming that absorption of energy is proportional to the electron density. In order to avoid radiation induced decomposition of products, the conversion was always kept below 0.1%.

The vapor phase experiments were carried out in cylindrical Pyrex cells (6 cm. diameter, 3.5 cm. length), which were closed off by a break seal. No G-values were determined.

Analysis.—After irradiation the cell was attached to an analysis system consisting of two traps, a modified Ward still and a Toepler pump. The H_2, CO, CH_4 fraction was removed at liquid nitrogen temperature and analyzed by combustion over hot cupric oxide. The hydrogen was determined by difference. The C_2 fraction was taken off at −175° and was analyzed for unsaturation by hydrogenation over a nickel catalyst.[8] The C_3, C_4 fraction which also contained acetylene was removed at −120° and analyzed with a mass spectrometer. No other products have been measured quantitatively in the course of this work.

Materials.—Acetone (Eastman Kodak Spectro Grade) was used as received. Methyl ethyl ketone and diethyl ketone (Eastman Kodak) were fractionated with rejection of large head and tail fractions. Diphenylpicrohydrazyl (DPPH) was obtained from Aldrich Chemical Co. and was kept under vacuum before being introduced into the cell.

Results

Liquid Phase.—Table I represents the G-values of the major volatile products formed in the liquid phase radiolysis of acetone. These results can be summarized as follows: 1. The carbon monoxide, methane, ethane and hydrogen yields vary only slightly with temperature from −80 to 27°. A rather pronounced increase takes place at temperatures above 27°. 2. The G-values of carbon monoxide, methane and ethane are slightly higher for light than for heavy acetone, while $G(H_2)/G(D_2) = 2$ at 27°. 3. Addition of iodine or DPPH in concentrations between 1 and 2.5×10^{-2} M leads to 85% reduction in the methane yield, while at 27° carbon monoxide, ethane and hydrogen are reduced by approximately 20%. DPPH concentrations above $5 \times 10^{-2}M$ reduced the yields of all products without affecting the relative ratios. 4. For the experiments employing equimolar mixtures of acetone + acetone-d_6, the ratio $(CH_4 + CD_3H)/(CD_4 + CH_3D)$ corresponds to a value of 7.3 in absence of scavengers as compared to a value of 1.2 in presence of $2.5 \times 10^{-2}M$ DPPH. The ethanes C_2H_6, CH_3CD_3, C_2D_6 were formed in the ratio 1:0.65:0.50. This ratio remained practically unchanged upon addition of DPPH.[9] H_2, HD and D_2 were formed in the ratios 4.3:2.8:1.0. 5. Various minor products were found to be formed: C_2H_2, C_2H_4, C_3H_4, C_3H_6, C_3H_8. The G-values of these products were less than 0.02 and were only slightly affected by addition of iodine.

The major volatile products formed in the liquid phase radiolysis of methyl ethyl ketone are given in Table II. It can be seen that $G(CO)$ and $G(CH_4)$ are approximately equal and that both increase with temperature. $G(C_2H_6)$ is larger than $G(CH_4)$ and does not vary in the temperature region −80 to 72°. Scavengers reduce the methane and ethane yields considerably, while the carbon monoxide, propane and butane yields are only slightly reduced. $G(H_2)$ is lowered upon addition of iodine and DPPH by, respectively, 25 and 20%.

$G(CO)$ is considerably higher in the radiolysis of diethyl ketone than in the radiolysis of acetone and methyl ethyl ketone. Addition of scavengers reduces the CO yield to about half the amount formed at 27° in absence of scavengers.

Minor products such as C_2H_8, C_3H_4, C_3H_6, C_4H_8 were detected in the radiolysis of both compounds. Although no impurities could be found by vapor phase chromatography, undistilled methyl ethyl ketone produced large quantities of butene (G = 1) without however affecting the other products. The butene yield was the same in presence and in absence of iodine. In the radiolysis of undistilled diethyl ketone, CO_2 was found to be a major product. Addition of iodine reduced the CO_2 yield, but butene and pentene were formed instead. By using freshly fractionated ketones, CO_2 and butene were both reduced to trace amounts.

Vapor Phase.—The results of a few vapor phase experiments at 110 ± 5° are given in Table III. The products are essentially the same as those found in the liquid phase radiolysis, although the ratios in which they are formed are different.

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(7) R. H. Schuler and A. O. Allen, *J. Chem. Phys.*, **24**, 56 (1956).

(8) A. Shepp and K. O. Kutschke, *Can. J. Chem.*, **32**, 1112 (1954).

(9) The estimates of these ratios are not better than within 10%, in view of the presence of partially and fully deuterated ethylenes.

TABLE II

LIQUID PHASE RADIOLYSIS OF METHYL ETHYL KETONE AND DIETHYL KETONE

	Scavenger	T, °C.	Time, min.	G (molecules/100 e.v.) CO	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_4H_{10}
$CH_3COC_2H_5$		−80	240	0.713	1.18	0.78	2.73	0.445	0.346	0.208
		27	636	0.83	1.2	0.85	2.77	.47	.420	.170
		72	510	1.10	1.2	1.12	2.70	.46	.515	.215
	2×10^{-2} M (DPPH)	27	400	0.77	1.0	0.19	0.25	.42	.35	.185
	10^{-2} M (I_2)	27	600	0.74	0.87	0.20	0.155	.405	.34	.190
$C_2H_5COC_2H_5$		27	604	1.52	1.22	0.12	3.95	0.53		0.335
		65	515	1.94	1.25	.16	4.34	.54		.350
		92	711	2.41	1.26	.13	4.80	.55		.45
	2×10^{-2} M (DPPH)	92	574	0.89	1.17	.08	0.61	.54		.36
	2×10^{-2} M (DPPH)	27	471	.77	1.16	.07	.35	.56		.32
	10^{-2} M (I_2)	27	590	.75	0.94	.05	.20	.59		.30

Minor products such as acetylene and propylene are formed in relatively higher yields than in the liquid phase radiolysis. Acetaldehyde and propionaldehyde were found in the products of the methyl ethyl ketone and diethyl ketone radiolyses.

TABLE III

VAPOR PHASE RADIOLYSIS OF KETONES

$T = 110 \pm 5°$, $P = 70$ cm.

Compound	Rates, cc./min. × 10^5 H_2	CO	CH_4	C_2H_6	C_2H_4	C_3H_8	C_4H_{10}	C_2H_2
CH_3COCH_3	2.5	3.2	6.7	0.33	0.16	0.05	0.01	0.19
$CH_3COC_2H_5$	4.40	3.02	3.5	4.6	1.65	.12	.07	.2
$C_2H_5COC_2H_5$	4.8	3.1	0.8	8.7	1.65	.05	.16	.18

Discussion

Radiation probably leads to the formation of excited and ionized ketone molecules along the track. Nothing definite can be said about the fate of the ions. In the liquid phase, Samuel and Magee's[10] theory favors a recapture of the electron by the parent ion. This would result in the formation of a highly excited molecule. Ion–molecule reactions have received much attention, and it has been pointed out that they cannot be neglected in the interpretation of certain vapor phase data.[11]

Because the data given in this paper do not provide a clear indication on how important excited molecule decompositions are as compared to ion–molecule reactions, only over-all processes will be presented. It will be shown that most of the products can be explained on the basis of well known radical reactions.

Acetone.—The fact that methane formation is largely prevented by scavengers indicates that methyl radicals are present and that at least 85% of the methane is formed by an abstraction reaction from acetone

$$CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3 \quad (1)$$

The data on the radiolysis of equal CH_3COCH_3–CD_3COCD_3 mixtures provides some information about the hydrogen abstraction. If all methyl radicals were thermalized before they abstract a H or D atom from acetone, a value of 13[12] would be expected for the ratio $(CH_4 + CD_3H)/(CD_4 + CH_3D)$. Actually, values of 7.3 and 1.2 were obtained, respectively, in absence and in presence of scavengers. Subtraction of the methanes not taken out by DPPH leads to a value of 13.7 for this ratio. This may be considered as evidence for the fact that the methanes, except for those not reduced by scavengers, were formed by a normal thermal abstraction reaction.

The equality of the CD_4, CH_4, CD_3H and CH_3D yields for the run done in presence of DPPH can be explained by a hot radical reaction or by a sequence such as

$$CH_3COCH_3^+ + CH_3COCH_3 = CH_3COCH_4^+ + CH_3COCH_2$$

$$CH_3COCH_4^+ + e = CH_3CO + CH_4$$

In both cases an equal distribution of the methanes may be expected. A third possibility such as a disproportionation between methyl and acetyl radicals would lead to the same observation, but in view of the small rate compared to recombination, this reaction could only account for a small fraction of the methanes formed in presence of scavengers.

The formation of methyl radicals may be ascribed to at least two processes

$$CH_3COCH_3 \longrightarrow 2CH_3 + CO \quad (I)$$

$$\longrightarrow CH_3CO + CH_3 \quad (II)$$

The fact that the CO yield is only slightly reduced by addition of scavengers or by a reduction in temperature to −80° substantiates process I. This type of process, which may be written as a sequence of two steps, may lead to hot methyl radicals. The increase of the CO and methane yields at temperatures above room temperature may be considered as evidence for process II. The latter process is known to occur in the photolysis of acetone and has been ascribed to a triplet state decomposition. However collisional stabilization of a fraction of the excited acetyl radicals formed in process I would be another alternative to account for the presence of acetyl radicals.

A third process must be invoked to account for the hydrogen formed

$$CH_3COCH_3 \longrightarrow H + CH_3COCH_2 \quad (III)$$

The fact that the mass spectrum of acetone shows a 57 peak which is less than 1% of the 43 peak favors an excited molecule split. From these results little can be said about the fate of the acetonyl radicals formed in this process. However, acetic acid has been found to be a major product in the vapor phase radiolysis of acetone[13] from 27 up to 200°. This

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[10] A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

[11] D. P. Stevenson, *J. Phys. Chem.*, **61**, 1453 (1957).

[12] This value was deduced from extrapolated Arrhenius plots obtained in photolysis studies on CH_3COCH_3 and CD_3COCD_3.

[13] J. F. Paulson, doctoral dissertation.

can be accounted for, by assuming that acetonyl decomposes into ketene and methyl as a result of excess energy carried over in process III. This type of decomposition would also account for the fact that in the vapor phase radiolysis $^1/_2$ CH_4 + C_2H_6 is larger than CO. It may be expected that the H atoms formed in process III carry over a large excess of kinetic energy and also abstract with greater ease than methyl radicals. Both effects may explain the fact that a large fraction of the hydrogen is not taken out by scavengers.

Ethane is an important product in the liquid phase radiolysis of acetone although under these conditions normal diffusive recombination is of minor importance compared to abstraction. The fact that the ethane yield is relatively much smaller in the vapor phase radiolysis seems to exclude its formation in ion–molecule processes. The only small reduction of the ethane yield upon addition of scavengers seems to indicate that ethane is mainly formed by a recombination of methyl radicals in the track. Except for the fact that the C_2D_6 yield in the CD_3COCD_3 radiolysis is lower than the C_2H_6 yield in the CH_3COCH_3 runs, no obvious interpretation can be given for the distribution of the ethanes in the radiolysis of equimolar mixtures of acetone and acetone-d_6.

Methyl Ethyl Ketone.—The reduction of the methane and ethane yields by scavengers indicates that both compounds are largely formed by reactions involving radicals. By analogy with the acetone experiments, two abstraction reactions may be considered as the main sources of methane and ethane

$$CH_3 + CH_3COC_2H_5 = CH_4 + CH_3COC_2H_4$$
$$C_2H_5 + CH_3COC_2H_5 = C_2H_6 + CH_3COC_2H_4$$

The run at −80° as well as the experiments performed in presence of scavengers, indicate that process IV occurs with a G value of 0.73 ± 0.03.

$$CH_3COC_2H_5 \longrightarrow CH_3 + CO + C_2H_5 \qquad (IV)$$

The increase of the CO and CH_4 yields with temperature may be considered as evidence for process V

$$CH_3COC_2H_5 \longrightarrow CH_3CO + C_2H_5 \qquad (V)$$

A process such as

$$CH_3COC_2H_5 \longrightarrow CH_3 + C_2H_5CO$$

does not have to be considered in view of the fact that $G(C_2H_6)$ remains practically unchanged with temperature, while $G(CH_4) = G(CO)$ at all temperatures. In this respect there seems to be some analogy with the liquid phase photolysis of methyl ethyl ketone, where it was found that methyl ethyl ketone decomposed mainly into acetyl and ethyl radicals.[3]

The formation of ethylene in both the vapor and liquid phase radiolysis in presence and in absence of scavengers can be explained by the occurrence of process VI

$$CH_3COC_2H_5 \longrightarrow CH_3CHO + C_2H_4 \qquad (VI)$$

Ethylene was also found to be a product in the short wave length photolysis of methyl ethyl ketone and diethyl ketone in presence of scavengers.[14] A small fraction of the ethylene is formed probably by a process analogous to the one which is responsible for the ethylene found in the acetone radiolysis. The contribution of the disproportionation reactions

$$CH_3 + C_2H_5 = CH_4 + C_2H_4$$
$$C_2H_5 + C_2H_5 = C_2H_6 + C_2H_4$$

amounts to at most 10 and 4% of the ethylene[15,16] formed, respectively, in the liquid and vapor phase radiolysis. Disproportionation between acetyl and ethyl radicals may increase the liquid phase value to some extent. Another source of ethylene may be a process such as

$$CH_3COC_2H_5 \longrightarrow H + CH_3COC_2H_4 \qquad (VII)$$

where $CH_3COC_2H_4$ decomposes into acetyl and ethylene as result of excess energy carried over in this process. H atoms should split off mainly from α-carbons, so that the resulting radicals will eventually decompose into methyl ketene and methyl or into ketene and ethyl. Decompositions of this type might explain the fact that in the vapor phase radiolysis the ethane and methane yields are both larger than the CO yield. The higher hydrogen yields in the liquid and vapor phase radiolysis of methyl ethyl ketone and diethyl ketone as compared to acetone can be attributed to the presence of weaker bonded secondary H atoms.

The formation of appreciable amounts of propane and butane, both in the presence and absence of scavengers can be explained by a recombination of alkyl radicals in the track. The presence of butane would indicate that recombination may occur from radicals originating from different molecules. The formation of propane and butane in the track in presence of the high DPPH concentrations used in this work, conflicts with Chapiro's interpretation of his intensity *versus* critical DPPH concentration plots.[17]

Diethyl Ketone.—The diethyl ketone data can be interpreted in the same way as the acetone and methyl ethyl ketone results. The higher CO and ethane yields are no doubt due to the fact that a large fraction of the propionyl radicals formed in

$$C_2H_5COC_2H_5 \longrightarrow C_2H_5 + C_2H_5CO$$

process undergoes thermal decomposition. This is in agreement with liquid phase photolysis data,[3] where it was found that at temperatures above 90° all propionyl radicals were decomposed. Addition of scavengers reduces the CO yield to practically the same value as the one found in the acetone and methyl ethyl ketone radiolyses. This indicates that decomposition into CO and two alkyl radicals takes place at the same yield for the three ketones. In this connection it may be pointed out that appreciably lower CO yields were obtained in the liquid phase radiolysis of ketones with γ-hydrogens. For instance, at 27° and in presence of scavengers, values of 0.48 and 0.40 were obtained, respectively, in the radiolysis of methyl n-propyl ketone and methyl n-butyl ketone[18] as compared to 0.74 ±

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(14) P. Ausloos, to be published.

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

(16) P. Ausloos and E. W. R. Steacie, *ibid.*, **33**, 1062 (1955).

(17) A. Chapiro, *J. chim. phys.*, **51**, 165 (1954).

(18) P. Ausloos, unpublished results.

0.02 for the other ketones. This is analogous with the results of photochemical studies, where it was found that ketones containing γ-hydrogens have a primary quantum yield less than unity[19,20]. The low quantum yield was attributed to an internal degradation of the energy in the molecule. In this connection it may be mentioned that ethylene and propylene were major products in the radiolysis of methyl *n*-propyl ketone and methyl *n*-butyl ketone, respectively.[18] This is in analogy with photolysis data and the mass spectra cracking pattern of these compounds.

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[19] W. Davis, Jr., and W. A. Noyes, Jr., THIS JOURNAL, **69**, 2153 (1947).

[20] C. R. Masson, *ibid.*, **74**, 4731 (1952).

[CONTRIBUTION FROM THE INSTRUMENT DIVISION, VARIAN ASSOCIATES, AND THE CHEMISTRY DEPARTMENT, MICHIGAN STATE UNIVERSITY]

Nuclear Magnetic Resonance Spectra of Steroids

BY J. N. SHOOLERY[1] AND MAX T. ROGERS[2]

RECEIVED APRIL 21, 1958

The high resolution nuclear magnetic resonance spectra of forty-seven steroids have been obtained and a number of peak positions have been measured with an accuracy of approximately 1 c.p.s. relative to the resonance of pure benzene. Empirical correlation of the data with the known steroid structures has allowed the assignment of characteristic group frequency shifts to a number of chemical functional groups. The applicability of these shifts to analysis of unknown steroids is discussed. Axial and equatorial protons in the 3-position are found to be shifted apart more than 20 c.p.s., and 18 ± 5 c.p.s. in the 11-position. Finally, the sensitivity of this method of analysis is discussed and found to be adequate to permit samples of a few milligrams to be studied.

Introduction

During the past few years an increasing number of laboratories have begun to apply the high resolution nuclear magnetic resonance (n.m.r.) technique to the solution of chemical structure problems. A general understanding of the experimental conditions which must be satisfied in order for useful spectra to be obtained is becoming more widespread. However, two of these conditions have often been believed to be more stringent than is actually the case. These are, first, the requirement of rapid random molecular motional averaging of direct dipole–dipole broadening which leads to the necessity for a liquid sample and, second, the need for a fairly high concentration of the molecular species being studied in order to achieve a useful signal-to-noise ratio. As a result, there has been a tendency to regard molecules in the molecular weight range from 300 to 500 as difficult to study *via* high resolution n.m.r. techniques, and above 500 as virtually impossible. However, the early studies from which such conclusions were drawn were usually concerned with long chain hydrocarbons which are viscous liquids, or polynuclear aromatic compounds which are too high melting for study without recently developed high temperature apparatus[3] and too insoluble in solvents with low proton backgrounds. Recent work[4] has shown that diluting viscous liquids with several volumes of a proton-free, low-viscosity solvent does, indeed, often permit enough molecular motional averaging to occur, even at room temperature, to give acceptably narrow resonance lines. The same results might be expected to hold for dilute solutions of normally solid substances of comparable molecular weight. The present study was carried out to find suitable experimental conditions under which sufficiently well resolved spectra of steroids could be obtained to permit assignments to be made, to assign the resonance peaks wherever possible and to correlate the assignments with the structural features of the steroid molecules.

For reasons described later it was desirable to obtain all of the spectra in the same solvent. Chloroform possesses the necessary solvent properties and its single sharp resonance does not interfere with the resonances of any of the steroids employed in this study, but even the spectrophotometric grade offered commercially gives a whole spectrum of impurity peaks which are comparable in size to many of the signals from the solute. If suitable purification techniques were employed, chloroform could be used successfully as a solvent. It is easier, however, to use deuterated chloroform which is commercially available and which is completely free of background interference.

The optimum concentration for this work lies in the vicinity of a 0.5 *M* solution. Such a solution is obtained from 50 to 75 mg. of steroid (depending on the molecular weight) dissolved in 0.4 cc. of $CDCl_3$, a typical cell volume. An encouragingly large number of steroids are soluble to this extent and if acetate derivatives are prepared most others can be made to fall into this category. Higher concentrations are likely to lead to excessive viscosity with consequent line broadening and are often too demanding on the amount of pure compound available. Lower concentrations make difficult the measurement of the positions of certain broad, low peaks in the spectrum which are among the more important chemical shift measurements which may be desired; however, this loss of signal-to-noise ratio is offset by several compensating factors, among which might be mentioned diminished viscosity

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[1] Instrument Division, Varian Associates, Palo Alto, California.

[2] Michigan State University, East Lansing, Michigan.

[3] J. N. Shoolery and J. D. Roberts, *Rev. Sci. Instr.*, **28**, 61 (1957).

[4] Unpublished studies, Varian Associates.