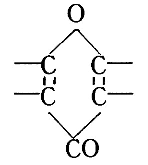
29. *Studies in Dielectric Polarisation. Part V. Benzene Solutions of Pyrones, Thiopyrones, and Thioketones. Dioxan Solutions of Ureas and Thioureas.*

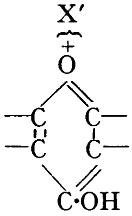
By Eric C. E. Hunter and James R. Partington.

An important difference between oxygen and sulphur is exhibited in the relatively much greater ease with which the latter element can increase in valency by co-ordination or by the formation of charged ions (Part I; J., 1931, 2062). The present communication extends our previous studies in this field and deals with some ketonic and thioketonic compounds. The apparatus used was that described in Part II (J., 1932, 2812).

The results for the γ-pyrones are of interest in relation to the well-known basic properties of these compounds. The constitution of the salts of γ-pyrones (I) has been the subject of much investigation and discussion (Henrich, " Theories of Organic Chemistry," 1922, 552; Knox and Richards, J., 1919, **115**, 508; Gibson and Simonsen, J., 1928, 2309), which largely centred on the question as to whether addition of acid occurred on the ethereal or the ketonic oxygen, and the solution of the problem was considerably advanced when Kehrmann and Duttenhöfer (*Ber.*, 1906, **39**, 1299) obtained a well-defined iodide from the yellow syrup resulting from the interaction of methyl sulphate and dimethylpyrone. Baeyer (*Ber.*, 1910, **43**, 2337; cf. Hofmann, *ibid.*, p. 2624; Decker and von Fellenberg, *Annalen*, 1907, **356**, 281; Robinson, J., 1916, **109**, 1041) found that a readily crystallisable perchlorate was formed by the addition of perchloric acid to the yellow syrup, and that both the perchlorate and the iodide on treatment with ammonium carbonate solution in the cold gave immediately methoxylutidine. The conclusion was drawn that the pyrone salt has a benzenoid structure (II), although the normal reaction between pyrones and ammonia is to replace oxygen in the ring by NH, and not N.

(I.)





(II.)

Physicochemical experiments (Walden, *Ber.*, 1901, **34**, 4189; 1902, **35**, 1242; Sackur, *ibid.*, 1902, **35**, 1242; Rördam, *J. Amer. Chem. Soc.*, 1915, **37**, 557) showed that dimethyl-γ-pyrone is a very weak base, or an amphoteric electrolyte, its salts being largely hydrolysed in aqueous solution. This result was confirmed, and a comparison of the basic strengths of dimethyl-, diphenyl-, and phenylmethyl-γ-pyrones determined, by Mitchell and Partington (J., 1929, 1862) and Johnson and Partington (J., 1931, 86). The following values for the basic constant $K = [\mathrm{B{\cdot}H^{\cdot}}][\mathrm{H_2O}]/[\mathrm{H_3O^{\cdot}}][\mathrm{B}]$, were found: Ethyl alcohol 0·18; γ-pyrone 0·548; diphenyl-γ-pyrone 1·25; phenylmethyl-γ-pyrone 1·83; dimethyl-γ-pyrone 2·74. From these values of K the general relation between the electrochemical character of the substituent (W. A. Noyes, *Ber.*, 1924, **57**, 1233) and the basic strength is seen to be what would be anticipated.

The evidence supports formula (II) for the pyronium ion, hydrion of $\mathrm{H^{\cdot}X'}$ having added to the carbonyl group to form a structure like a tertiary alcohol (cf. Robinson, J., 1916, **109**, 1041). There is much other evidence (which cannot be fully considered here) that hydrion co-ordination takes place, if at all, with great difficulty on an ethereal or ketonic oxygen when present alone in a molecule, so that the possibility of rearrangement in the rest of the molecule, *e.g.*, of the γ-pyrone (I), is of importance.

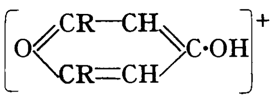
The availability of hydrogen chloride in alcohol, as measured, *e.g.*, by its catalytic effect, is unaffected by the presence of ethyl ether (Partington, J., 1910, **97**, 19; Mitchell and Partington, J., 1929, 1862), methyl ether (Mitchell and Partington, *ibid.*), di-*n*- and -*iso*-propyl ethers, furan (Johnson and Partington, J., 1931, 86), and acetone (Lapworth, J., 1908, **93**, 2199). The lower dipole moment ($0{\cdot}63 \times 10^{-18}$) of furan as compared with an aliphatic open-chain ether, shows that appreciable interaction occurs owing to the presence of the double bonds in the former molecule (see Part I., p. 2070). This interaction probably leads to a diminution of negative charge on the oxygen, so that the basic properties of the latter are inhibited. The simultaneous presence of ethereal and ketonic oxygen in the ring, as in the γ-pyrones, confers basic properties, since now the ethereal oxygen may acquire a positive charge owing to rearrangement of the double linkages in the ring (cf. Hewitt, J., 1902, **81**, 663; Ghosh, J., 1915, **107**, 1588). The ethereal oxygen is acting as a source of electrons, and unless a suitable receiver of these is also present, no basic function is assumed by the molecule. We think it useful to draw attention to these considerations, already advanced on purely chemical grounds [Robinson, " Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," Institute of Chemistry, 1932, p. 15], since the physicochemical investigations to which reference is made can be satisfactorily explained by them.

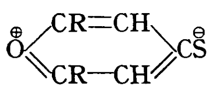
The extensive series of experiments on the formation of supposed oxonium compounds from ether and other oxygen compounds such as cineol, and complex acids, made by Baeyer and Villiger (*Ber.*, 1901, **34**, 2679, 3612; 1902, **35**, 1201) are not at all satisfactory from the point of view of modern physicochemical research, and the large mass of material collected is in need of complete revision (cf. Holleman, " Text-book of Organic Chemistry," 1930, p. 296; Hantzsch, *Ber.*, 1919, **52**, 1543).

Apart from the existence of solid hydrates of inert gases, the large number of anomalous salt hydrates (Ephraim, " Chemische Valenz und Bindungslehre," 1928, 127, 229 ff., 243) makes any general application of the present theories of valency difficult. A tendency to produce electroneutrality in small regions, which apparently operates in ion association in crystals (Pauling, *J. Amer. Chem. Soc.*, 1929, **51**, 1010), is very probably also involved in the association of molecules possessing dipoles to form solid aggregates, but the mechanism is at present too vague to permit of useful application. The crystal structures of NH_4ClO_4 and $HClO_4,H_2O$ are in agreement with the supposition that in the latter the ions $H_3O^{\cdot}$ and ClO_4' are present (Volmer, *Annalen*, 1924, **440**, 200).

Spectroscopic evidence (Hantzsch, *Ber.*, 1919, **52**, 1535, 1544) indicates that the salts of dimethylpyrone and dimethylthiopyrone exist in two chromoisomeric forms, as is the case for the simple ammonium, phosphonium, and sulphonium compounds. The colourless forms are true salts, corresponding with those of pyridine, and their ultra-violet absorption spectra indicate the presence of a benzenoid structure. Since dimethylthiopyrone is coloured, owing to the presence of the CS chromophore, and its salts are colourless, Hantzsch concluded that, in the latter, the thioketo-group has disappeared. These conclusions find support in the work of Arndt, Scholz, and Nachtwey (*Ber.*, 1924, **57**, 1903) and Arndt and Lorenz (*ibid.*, 1930, **63**, 3121), who suppose the colourless pyronium ion to be (III) and write dimethylthiopyrone as internally ionised as in (IV) : Salt formation then occurs by co-ordination of hydrion at the $>C-\overset{\ominus}{O}$ or $>C-\overset{\ominus}{S}$ group, which groups are the seats of powerful electric fields. Once the C–OH or C–SH group is formed, it differs in no respect from a carbinol or thiocarbinol group.

(III.)





(IV.)

This aspect of the structure of pyrone compounds involves the instability of the conventional keto- and thioketo-groups. The latter are especially unstable, since the aliphatic thioketones $R_1R_2C{=}S$ exist in stable trimeric modifications only, and show *cis-trans*-isomerism, pointing to the formation of a six-membered ring in which the $C{=}S$ group has disappeared (Baumann and Fromm, *Ber.*, 1891, **24**, 1419).

Monomeric thioketones occur in the aromatic series, *e.g.*, thiobenzophenone, where the phenyl group stabilises this form. These compounds are still very reactive, forming trisulphides by atmospheric oxidation (Schönberg, Schütz, and Nickel, *Ber.*, 1928, **61**, 2175), and the replacement of phenyl by hydrogen or alkyl groups promotes association

(Schönberg, *Ber.*, 1929, **62**, 195). The greater deformability of sulphur as compared with oxygen (see Parts II—IV; J., 1932, 2812) makes it very susceptible to the fields of other groups. The C=S group is a strong chromophore, thiobenzophenone being deep blue. Introduction of auxochrome groups, such as OMe, however, does not deepen the colour, and thiodi-*p*-methoxybenzophenone is lighter in colour. This is explained by Bergmann, Magat, and Wagenberg (*Ber.*, 1930, **63**, 2576) on the assumption that thiobenzophenone is a free radical, which agrees with its capacity of forming a peroxide:

$$\mathrm{Ph_2\overset{\vdots}{C}—\overset{\vdots}{S}.}$$

EXPERIMENTAL.

Preparation of Materials.—C_6H_6 was purified as in Part I. Dioxan was dried by refluxing with Na wire until no action occurred on adding excess Na. This was found necessary in order to remove any uncyclised glycol. The product was then carefully fractionated and frozen until of const. density. Of two specimens, both purchased from British Drug Houses Ltd., one had $D^{20°}_{4°}$ 1·0330, the other 1·0340. It was found impracticable to purify the dioxan of $D^{20°}_{4°}$ 1·0330 beyond this limit. In any case, this specimen was suitable for use as a solvent. The ureas were purchased and used direct. Thiodimethyl-γ-pyrone was prepared from dimethyl-γ-pyrone (purchased from British Drug Houses Ltd.) according to the method of Hantzsch (*Ber.*, 1919, **52**, 1535). Thiobenzophenone was made according to the method described in "Chemical Syntheses" (1931, Vol. XI, p. 94). The specimen of diphenyl-γ-pyrone was identical with that used by Johnson and Partington (J., 1931, 86) and was kindly placed at our disposal by Mr. Johnson.

Results.—The electronic polarisations, P_E, of the solids were calc., as usual, from the sum of the at. refractions (Smyth, Engel, and Wilson, *J. Amer. Chem. Soc.*, 1929, **51**, 1736). Since the orientation polarisation of the compounds is in every case large, above 200 c.c., a small error in P_E will not sensibly affect the value of the dipole moment. The symbols and methods of calculation employed are the same as those used in previous communications.

It should be pointed out that the bond angle 90° for H_2S adopted in Part II on the basis of Raman spectrum observations by Dadieu and Kohlrausch, had already been deduced theoretically by Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 1376). The Raman spectra indicate that the C–S linkages in thiophen, mercaptans, and alkyl sulphides have practically the same characteristic vibrations, and the S–H linkage vibration is identical with that in H_2S (Crigler, *J. Amer. Chem. Soc.*, 1932, **54**, 4199).

I. *Benzene Solutions.*

f_1.	f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.
Dimethylpyrone, m. p. 132°.				
0	1	0·8785	2·277	26·52
0·00871	0·99129	0·8805	2·502	29·73
0·00998	0·99002	0·8809	2·513	29·88
0·01512	0·98488	0·8827	2·666	31·84
0·01979	0·98021	0·8850	2·806	33·53
Diphenylpyrone, m. p. 139—140°.				
0	1	0·8785	2·277	26·52
0·0043	0·9957	0·8814	2·375	28·09
0·0052	0·9948	0·8820	2·377	28·20
Dimethylthiopyrone, m. p. 146°.				
0	1	0·8785	2·281	26·58
0·00349	0·99651	0·8794	2·412	28·46
0·00597	0·99403	0·8804	2·513	29·89
0·00983	0·99017	0·8821	2·679	31·98
0·01607	0·98393	0·8841	2·903	34·70
Thiobenzophenone, m. p. 52—53°.				
0	1	0·8785	2·281	26·58
0·00362	0·99638	0·8801	2·340	27·57
0·00675	0·99325	0·8817	2·394	28·40
0·01382	0·98618	0·8850	2·510	30·19
Dioxan, m. p. 9·8—10·2°.				
0	1	0·8785	2·281	26·58
0·0563	0·9437	0·8867	2·282	26·36
0·1107	0·8893	0·8943	2·284	26·54
0·1879	0·8121	0·9065	2·293	26·53

II. *Dioxan Solutions.*

f_1.	f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.
s-Dimethylurea, m. p. 101°.				
0	1	1·0330	2·316	26·00
0·00240	0·99760	1·0330	2·404	27·18
0·00365	0·99635	1·0331	2·451	27·79
0·00683	0·99317	1·0332	2·567	29·24
0·00902	0·99098	1·0333	2·638	30·10
s-Diethylthiourea, m. p. 76°.				
0	1	1·0340	2·320	26·01
0·00350	0·99650	1·0346	2·450	27·78
0·00818	0·99182	1·0350	2·615	29·89
0·01286	0·98714	1·0351	2·842	32·55
0·01359	0·98641	1·0353	2·856	32·73
0·01943	0·98057	1·0356	3·126	35·61
Carbanilide (40°), m. p. 238°.				
0	1	1·0120	2·278	25·98
0·00196	0·99804	1·0129	2·334	26·83
0·00321	0·99679	1·0135	2·374	27·42
0·00355	0·99645	1·0136	2·381	27·52
Thiocarbanilide (20°), m. p. 153°.				
0	1	1·0330	2·316	26·003
0·00289	0·99711	1·0343	2·422	27·524
0·00463	0·99537	1·0352	2·487	28·400
0·00675	0·99325	1·0363	2·560	29·407
0·01142	0·98858	1·0382	2·725	31·522
0·01225	0·98775	1·0389	2·765	32·016
0·01835	0·98165	1·0414	2·967	34·640

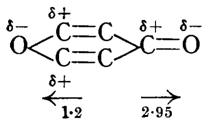
III. *Summary of Results.*

	P_2.	P_E.	P_O.	$\mu \times 10^{18}$.
Dimethyl-γ-pyrone	385	35*	350	4·05
Diphenyl-γ-pyrone	380	72	308	3·82
Dimethylthio-γ-pyrone	580	41	539	5·05
Thiobenzophenone	304	63	241	3·37
Dioxan	26	21·7*	4·3	0·40
s-Dimethylurea	520	27	493	4·8
s-Diethylthiourea	545	43·5	501·5	4·9
Carbanilide (40°)	480	65	415	4·6
Thiocarbanilide	570	72*	498	4·85

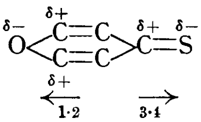
* Measurements made of the refraction of the liquid or solution. Owing to the sparing solubility of the substances, the results for the ureas and thioureas are liable to an error of ± 0·1 unit.

DISCUSSION OF RESULTS.

The values of the dipole moments show that the pyrones and thiopyrones do not contain the ether and keto- (or thio-ether and thio-keto-) groups, as had been concluded previously from the chemical evidence, since, if this were so, the resultant moments would be expected to be the algebraic sums of the group moments :



$\mu = 1·75$ calc. (obs. 4·05 for dimethylpyrone).



$\mu = 2·2$ calc. (obs. 5·05 for dimethylthiopyrone).

The C=O moment is taken as that of benzophenone, 2·95 (Donle and Volkert, *Z. physikal. Chem.*, 1930, *B*, **8**, 60) ; the C=S moment, that of thiobenzophenone 3·4 (present paper), and the $\mathrm{O}\!<^{\mathrm{C}}_{\mathrm{C}}$ moment that of an ether (see Part III). The measured moments of the pyrones and thiopyrones, which are much greater than these calculated values, point to the presence of polar bonds, as in the structure assigned to them by Arndt and co-workers [see formulæ (III) and (IV) above].

It is noteworthy that, in the case of compounds containing sulphur and oxygen united only to carbon, the dipole moment of the C–S bond is greater than that of the C–O bond. This has been found by us to be true for the ethers and sulphides, and is supported by the data presented in this paper. In the case of doubly bound sulphur and oxygen, the following results have been found (all multiplied by 10^{18}).

CO_2 $\mu = 0$ (Stuart, *Physikal. Z.*, 1928, **47**, 457).
COS, $\mu = 0·65$ (Miles and Zahn, *Physical Rev.*, 1928, **32**, 497).
Benzophenone, $\mu = 2·95$ (Donle and Volkert, *loc. cit.*).
Thiobenzophenone, $\mu = 3·4$ (present work).
Dianisyl ketone, $\mu = 3·9$ (Donle and Volkert, *loc. cit.*).
Dianisyl thioketone, $\mu = 4·4$ (Donle and Volkert, *loc. cit.*).

SUMMARY.

The dipole moments ($\mu \times 10^{18}$) of dimethyl-γ-pyrone (4·05), diphenyl-γ-pyrone (3·82), dimethylthio-γ-pyrone (5·05), thiobenzophenone (3·37), dioxan (0·40), *s*-dimethylurea (4·8), *s*-diethylthiourea (4·9), carbanilide (4·6), and thiocarbanilide (4·85) have been determined. The chemical properties of these compounds are discussed, as well as the mechanism of the formation of oxonium salts.

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