

Discussion.—The results on the alkali metals agree satisfactorily with the best previously published values, to within 0.2–0.5%.

The results on lithium hydride agree fairly well, the present value of the heat of hydrolysis being the highest. This higher value is explained if the sample used in this research is somewhat purer than the samples of the earlier workers. Thus, the heat of formation of lithium hydride seems to be established.

The heats of hydrolysis and formation of sodium hydride are less certain, owing to the relatively rapid rate of contamination of the finely divided samples by reaction with residual moisture in the dry-box atmosphere. The small batch size also necessitated the combination of data from several preparations, rather than their accumulation from one.

The heat of formation of sodium hydride of -13.60 kcal./mole agrees within experimental error with that of Hagen and Sieverts²⁰ of -12.8 , which was probably obtained on a purer sample than that of de Forcrand.¹⁹

Most of the previously published values for sodium and potassium hydrides are based upon dissociation pressure data in the region of 300 to 350°. These are undoubtedly accurate to $\pm 2\%$ at these temperatures, but their extrapolation to 25° is uncertain in the absence of high temperature heat capacity data for the hydrides. These uncertainties may be mainly responsible for the discrepancies for these compounds shown in Table II.

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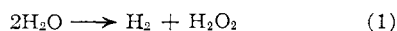
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The Radiation-induced Oxidation of Ferrous Ion

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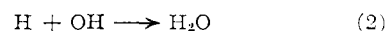
We should like to record our agreement with the remarks of Barr and King,¹ concerning the radiation chemistry of ferrous ion. We have also found² complete agreement between theory and experimental results if, in addition to the equations given previously,³ Allen's "molecular yield" process⁴



is also taken into account. Furthermore, the mechanism which has been suggested³ for the radiation-induced reaction in deaerated ferrous sul-

fate solutions has been confirmed by independent evidence obtained in a study of the photochemistry of ferrous sulfate solutions.⁵

In a recent paper, also dealing with the action of γ -rays on deaerated solutions of ferrous sulfate, Dewhurst⁶ has found that the initial yield of the ferrous oxidation is dependent upon ferrous salt concentrations and upon $p\text{H}$; an inspection of his results shows that this is so only at relatively low ferrous salt concentrations ($[\text{Fe}^{2+}] < 5 \times 10^{-3} M$) and at $p\text{H} > 1$. It should be pointed out that our mechanism is fully capable of explaining these results. It must be borne in mind that the mathematical equations given in our paper for the case of deaerated solutions have been derived, as stated there, under the assumption that interactions of radicals such as

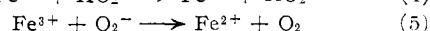
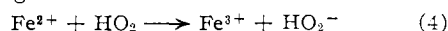


and recombination of hydrogen atoms



can be neglected. This assumption holds only when the ferrous salt and hydrogen ion concentrations are sufficiently high, and under these conditions excellent agreement is obtained with our kinetic equations. Under the conditions of Dewhurst's experiments (ref. 6), these interactions cannot always be neglected, as shown clearly by the dependence of the initial yield on the ferrous salt concentration. If, when appropriate, *e.g.*, the recombination of hydrogen atoms is taken into account, our theory leads directly to an explanation of the dependence of the initial yields on ferrous salt concentration and $p\text{H}$. (The $p\text{H}$ dependence of the reaction in deaerated solutions can be interpreted on the basis of a mechanism involving the H_2^+ ions; calculations carried out by Coulson⁷ have shown that the stability of this species in acid solution is fully compatible with theoretical expectations.)

In aerated ferrous sulfate solutions the situation regarding the initial $p\text{H}$ effect is not quite as clear. Dewhurst's experiments show that the initial oxidation yield is quite independent of the hydrogen ion concentration down to concentrations of $5 \times 10^{-2} M \text{H}_2\text{SO}_4$. On the basis of the present theory an initial dependence at higher $p\text{H}$'s, in a region of sufficiently low ferrous ion concentrations, may be due to interactions between the radicals in the clusters of high radical density, *e.g.*, $\text{O}_2^- + \text{OH} \rightarrow \text{O}_2 + \text{OH}^-$, with the dissociation equilibrium $\text{HO}_2 \rightleftharpoons \text{H}^+ + \text{O}_2^-$. On the other hand, an initial $p\text{H}$ dependence would also arise if a relatively large amount of ferric salt is initially present. The dependence of the oxidation yield on any ferric salt initially present is, of course, fully explained by our original mechanism, being simply due to the competition between the following two reactions



reaction (5) being favored as the $p\text{H}$ is increased.

Further experiments at different $p\text{H}$ and ferrous salt concentrations may be required to clear up this point. Otherwise all the experimental results can

(1) N. F. Barr and C. G. King, *THIS JOURNAL*, **76**, 5565 (1954).

(2) Cf. T. Rigg, Ph.D. Thesis, University of Durham, 1953.

(3) T. Rigg, G. Stein and J. Weiss, *Proc. Roy. Soc. (London)*, **211A**, 375 (1952).

(4) E. R. Johnson and A. O. Allen, *THIS JOURNAL*, **74**, 4147 (1952); H. A. Schwarz, J. T. Losee and A. O. Allen, *ibid.*, **76**, 4693 (1954).

(5) T. Rigg and J. Weiss, *J. Chem. Phys.*, **20**, 1194 (1952).

(6) H. A. Dewhurst, *Trans. Faraday Soc.*, **49**, 1174 (1953).

(7) C. A. Coulson, *Proc. Roy. Soc. (London)*, **211A**, 396 (1952).

be accounted for on the basis of the general theory proposed in our paper.

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The Electric Moments of Some Thiophene and Furan Derivatives

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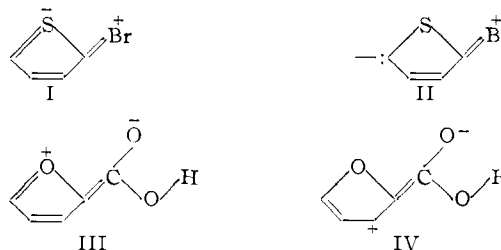
The electric moments of several derivatives of thiophene and furan have been reported in the literature¹⁻³ and it has been noted that group moments indicate a greater importance of conjugation of the substituent group with the thiophene or furan ring than with the benzene ring. We have, therefore, studied the electric moments of several substances in which an electron-donating or electron-receiving group is substituted in the thiophene or furan ring and have compared the observed values with those calculated from the group moments derived from observations on benzene derivatives.

Our values are in good agreement with those reported previously for 2-bromothiophene (1.37¹ and 1.36²), 2-iodothiophene¹ (1.14) and 2-methylfuran² (0.74). Nazarova and Syrkin³ report a lower value (1.38) for the moment of 2-furoic acid in benzene solution than we observe in dioxane solution. The comparison suggests that some association of the acid may occur in benzene solution. They report that cryoscopic data showed no appreciable association but present no data.

If the C-H moments are assumed to be 0.4 *D* (hydrogen positive) throughout, and the bond angles are taken from an electron diffraction report,⁴ the moment calculated for thiophene (0.52) is just equal to the observed value. The C-S bond moment is, then, essentially zero and a similar calculation for furan gives C-O = 0.25 *D* (oxygen negative) for the bond moment within the ring. Resonance with structures placing a positive charge on the hetero-atom is important in these molecules⁴ and reduces the normal C-O and C-S moments greatly. Moments were now calculated for the compounds studied here by use of the group moments and, for non-axial groups, the angles between the group moments and the bonds joining them to the ring, derived from an analysis of the available electric moments of benzene derivatives.⁵ A comparison of the calculated and observed values (Table I) reveals significant differences for the 2-halothiophenes, 2-*t*-butylthiophene and 2-furoic acid and agreement within experimental error for the remaining substances.

The C-Br and C-I group moments have been reduced from 1.10 and 0.90 in bromo- and iodo-

benzene to about 0.80 and 0.50 in 2-bromo- and 2-iodothiophene; comparable reductions occur in 2-bromo- and 2-iodofuran.³ An important contribution of structures analogous to I to the ground state of the molecule would account for the large effect observed since this structure is in addition to resonance forms of type II. In the halobenzenes only structures energetically more comparable to II can be written. The methyl and *t*-butyl group moments also appear to be somewhat larger in 2-methylthiophene³ and 2-*t*-butylthiophene (but not



in 2-methylfuran) than in toluene and *t*-butylbenzene. A significant contribution from (hyperconjugation) structures analogous to I and II would explain this effect although it is also possible that the ring carbon atoms are more electronegative than those in benzene thus altering the portion of the group moment attributable to electronegativity differences.

Electron-receiving groups show a similar, though relatively less important, tendency in that the carboxyl group moment is about 0.35 *D* larger in 2-furoic acid than in benzoic acid. A comparison of calculated electric moments with observed values in the literature¹⁻³ revealed similar increases in group moment for the nitro group in 2-nitrofuran and 2-nitrothiophene (0.15 *D*), the aldehyde group in furfuraldehyde and 2-thiophene aldehyde (0.4 *D*), and the acetyl group in 2-acetylthiophene (0.36). An appreciable contribution of structures of type III to the normal states of these molecules would account for the observed increments. Although more favorable than forms of type IV, these structures (III) are less favorable than those of type I because of the unfavorable charge distribution.

No electric moments of substituted thiophenols have been reported so the calculated moment of 3-mercaptothiophene (Table I) was derived from bond moments (C-S = 0.80, H-S = 0.84, ∠CSH = 100°). Because of the uncertainties in this calculation no particular significance can be attached to the agreement with the observed moment of 3-mercaptothiophene.

Experimental

Materials.—Benzene and Dioxane.—The purification and physical constants of the solvents have been reported.⁶

2-Bromothiophene.—A sample of 2-bromothiophene was the gift of the Michigan Chemical Co., St. Louis, Mich. It was dried and fractionated through an efficiently packed column, b.p. 63° (38 mm.), *n*_D²⁰ 1.5840, *d*₄²⁵ 1.7030.

2-Iodothiophene.—Eastman Kodak Co. White Label material was dried and fractionated, b.p. 88° (29 mm.), *n*_D²⁰ 1.6487, *d*₄²⁵ 2.0595.

2-Methylfuran.—A sample donated by the Quaker Oats Co. was dried and fractionated, b.p. 629° (760 mm.), *n*_D²⁰ 1.4302, *d*₄²⁵ 0.9093.

(1) L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948.

(2) R. Kesawani and H. Freiser, *THIS JOURNAL*, **71**, 218, 1789 (1949).

(3) L. M. Nazarova and Y. K. Syrkin, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 35 (1949); *Zhur. Obshchei Khim.*, **23**, 478 (1953).

(4) V. F. H. Schomaker and L. Pauling, *THIS JOURNAL*, **61**, 1769 (1939).

(5) M. T. Rogers, unpublished results.

(6) M. T. Rogers, *THIS JOURNAL*, **77**, 3681 (1955).