

respectively, the former number being considerably larger than the 1.37 obtained previously at 15°. ^{48,49}

It is clear from Fig. 3 that, compared to the simple Gross equation, the curve calculated from eq. 16 corresponds much more closely to the experimental data. While the fit is not as good as one would hope, it is difficult to say whether the difference is real or experimental. It is worth noting that the fit can be improved somewhat through the use of equations based on five or more equivalent exchangeable protons in the transition state. To illustrate, the rate ratio at $n = 0.5$ calculated from the equation derived for a transition state having five equivalent exchangeable protons is

(48) J. C. Hornel and J. A. V. Butler, *J. Chem. Soc.*, 1361 (1936).

(49) The difference between the values 1.37 and 1.57 cannot be ascribed to the different temperatures of the experiments. On the contrary, it is expected from theory⁵⁰ that the reaction in light water should have a higher activation energy and that consequently the k_D/k_H ratios for acid-catalyzed reactions should decrease with temperature, as it is actually found.^{50,51}

(50) M. Kilpatrick, *J. Am. Chem. Soc.*, **85**, 1036 (1963).

(51) P. Gross, H. Steiner, and F. Kraus, *Trans. Faraday Soc.*, **34**, 351 (1938).

1.196, compared with 1.18 (experimental) and 1.207 (eq. 16). For methyl acetate, the rate ratios calculated for $n = 0.5$ are 1.293 (simple Gross equation), 1.245 (eq. 16), and 1.236 ("fifth power equation") and are to be compared with the experimental ratio of 1.23. These results affirm the current view⁵² that acid-catalyzed ester hydrolysis is not to be considered representative of the simple A-2 category of mechanism.

In conclusion we wish to emphasize that the utility of rate measurements in H₂O-D₂O solvent mixtures appears to be somewhat limited by the relative insensitivity of k_n/k_H to mechanism, at least for acid-catalyzed reactions not involving slow proton transfer to carbon. However such data will continue to prove informative in certain cases, and this eventuality may now be decided beforehand for a particular reaction on the basis of the magnitude of k_D/k_H , the accuracy of the kinetics, the mechanistic possibilities to be considered, and the available independent information.

(52) J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4978 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND, COLLEGE PARK, MD.]

Ion Association in Polyvalent Symmetrical Electrolytes. VI. The Conductance of Manganese(II) Sulfate and Manganese(II) *m*-Benzenedisulfonate in Acetone-Water Mixtures at 25°

BY GORDON ATKINSON AND SERGIO PETRUCCI

RECEIVED JULY 1, 1963

The conductance of MnSO₄ has been measured in acetone-water mixtures up to 40% acetone and the conductance of Mn(*m*)BDS up to 70% acetone. All data were analyzed using the linearized Fuoss-Onsager equation to give Λ^0 , K_A , and a_j values. The behavior of these two salts shows marked specific solvent effects and is very similar to that in the previously measured methanol-water systems.

Recently the conductances of MnSO₄ and Mn *m*-benzenedisulfonate have been measured in both dioxane-water¹ and methanol-water mixtures.² The analysis of the data by the Fuoss-Onsager theory³ gave strong indications of specific solvent effects. The association constants, mean distance of closest approach parameters, and limiting conductances at infinite dilution all showed marked effects. Qualitative analysis of the data showed that both salts seemed to be closer to the idealized Bjerrum-Fuoss association behavior in the dioxane-water mixtures. In the methanol-water mixtures, all parameters showed drastic changes when the mole fraction methanol exceeded 0.25. This is the same point where the properties of the methanol-water solvent mixture show maximum deviations from ideal behavior. It looked as if the Mn salts considered the water-rich mixtures as being distinctly different solvents from the methanol-rich mixtures. This does not mean that such specific solvent interaction is only observed with high charge salts such as MnSO₄. However, the small deviations noted for 1-1 salts^{4,5} are greatly magnified by the enhanced ion-ion and ion-solvent forces in the 2-2 salt solutions. This is particularly true for transition metal ion salts. The recent advances in coordination chemistry⁶ have emphasized the greatly different metal-

ligand forces possible among ions of only slightly different ion radii. This difference in bond strength and character manifests itself both in the thermodynamics of metal-ligand interactions and in their kinetics.

It was decided to extend the previous work by examining the behavior of MnSO₄ and Mn(*m*)BDS in acetone-water mixtures. This solvent system was chosen because it was thought to exhibit a nonideal behavior similar to the methanol-water system. The acetone molecule possesses a dipole and so might be presumed capable of coordination with the ions. The Mn(*m*)BDS is essentially unassociated in water at 25° while the K_A for MnSO₄ is 133.

Experimental

The experimental technique is described in a previous publication by the authors.⁷ The Mn(*m*)BDS was a laboratory stock used in the previous work.^{2,3} It was dried over CaCl₂ at room temperature to the definite weighing form Mn(*m*)BDS·3.5H₂O. The MnSO₄ was C.P. material recrystallized twice from conductance water. Dried at 105°, it was used in the form MnSO₄·H₂O. This is a definite weighing form that is not particularly hygroscopic but is best maintained in a desiccator over anhydrous MnSO₄.

The acetone was dried over anhydrous CuSO₄ for 2 hr.⁸ and distilled through a 5-ft. fractionating column. The purity of the acetone was checked using its boiling point, refractive index, and dielectric constant. For each solvent mixture-salt combination, a batch of mixed solvent was prepared by weight. This same mixture was used for preparation of the concentrated stock solution and for the dilution run. The salt analyses were done as previously described.^{1,2}

(7) G. Atkinson and S. Petrucci, *J. Phys. Chem.*, **67**, 337 (1963).

(1) G. Atkinson and C. J. Hallada, *J. Am. Chem. Soc.*, **84**, 721 (1962).

(2) C. J. Hallada and G. Atkinson, *ibid.*, **83**, 3759 (1961).

(3) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959.

(4) (a) R. M. Fuoss and H. Sadek, *J. Am. Chem. Soc.*, **72**, 301, 5803 (1950); (b) R. M. Fuoss and E. Hirsch, *ibid.*, **82**, 1021 (1960); (c) S. Petrucci, *Acta Chem. Scand.*, **16**, 760 (1962).

(5) H. K. Bodenseh and J. B. Ramsey, *J. Phys. Chem.*, **67**, 140 (1963).

(6) E.g., "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, Chapter 1.

(8) "Organic Solvents," Vol. VII of "Techniques of Organic Chemistry," A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1955, p. 381.

Results

The conductance data are presented in Table I. The conductances and concentrations are not corrected for salt hydrolysis since the size of the corrections would

TABLE I
EXPERIMENTAL DATA^a

$C \times 10^4$	Λ	$C \times 10^4$	Λ
A. MnSO_4			
9.94% acetone		19.83% acetone	
2.1201	96.420	2.8420	74.901
4.7003	89.971	5.9016	67.089
8.9261	83.020	11.071	59.444
15.627	75.932	17.768	53.485
23.816	70.268	25.144	49.162
30.514	66.893	35.161	45.071
41.648	62.584	43.017	42.690
29.91% acetone		40.17% acetone	
3.6605	54.839	2.3767	42.787
7.2296	46.819	5.2157	34.038
12.969	40.033	9.1678	28.355
22.624	33.990	16.754	22.990
31.202	30.811	23.583	20.408
42.887	27.860	32.386	18.208
		40.006	16.877
B. $\text{Mn}(m)\text{BDS}$			
9.83% acetone		19.94% acetone	
2.0621	83.138	1.3304	71.843
4.1792	80.710	2.6870	69.841
7.3131	78.224	5.1566	67.234
10.366	76.375	7.7944	65.422
14.179	74.605	12.309	63.027
17.668	73.316	17.418	61.025
23.234	71.593	22.441	59.530
29.145	70.103	26.626	58.474
34.89% acetone		45.73% acetone	
2.0274	62.308	1.3462	59.478
3.6120	59.841	2.8386	55.687
6.2138	57.106	6.2941	50.569
10.888	53.813	9.1492	47.881
14.745	51.899	13.980	44.751
20.167	49.828	19.584	42.230
24.559	48.525	25.269	40.385
30.881	46.977	30.733	38.971
54.76% acetone		70.17% acetone	
3.7556	50.173	2.5409	44.234
6.3288	45.623	4.4752	38.385
10.447	41.240	8.2849	32.414
17.584	36.822	11.332	29.623
24.500	34.182	15.121	27.225
33.629	31.798	18.877	25.509
41.102	30.384		16.876
			19.971
			19.763
			18.980

^a Concentrations are in moles/l. and conductances in (ohm-cm.²-equiv.)⁻¹. C and Λ are reported to one more place than the authors feel is significant so that rounding-off errors can be avoided in recalculation.

be of the same order as the propagated experimental errors. The highest acetone concentrations for MnSO_4 and $\text{Mn}(m)\text{BDS}$ were 40 and 70%, respectively. This was determined by the rapidly decreasing solubilities of the salts. All the data were analyzed by the Fuoss-Onsager equation³ in the linearized form using no viscosity correction where the symbols and data treatment technique have been previously defined.^{1,2} The

$$\Lambda = \Lambda^0 - SC^{1/2}\gamma^{1/2} + EC\gamma \log C\gamma + JC\gamma - K_A f_{\pm}^2 \Lambda \gamma C$$

actual data treatment used to obtain K_A and Λ^0 was the "y-x" method of Fuoss as described previously.^{2,3}

The extended Debye-Hückel treatment was used to calculate the needed activity coefficients with the a° being obtained from the conductance J term. The need for an $(O)C^{3/2}$ term in the conductance equation for 2-2 salts noted in an earlier paper⁷ caused little error in the data analysis in this work. This is because of the low ionic concentrations in the mixtures of lower dielectric constant than water. The lack of actual viscosity data on these systems makes the application of a totally theoretical viscosity correction term seem too arbitrary for such highly charged ions.

The parameters resulting from the data analysis are given in Table II. The solvent properties used for the

TABLE II
CALCULATED PARAMETERS

Acetone, %	D	$\eta \times 10^2$	Λ^0	$\Lambda^0\eta$	K_A	$a_J(\text{\AA})$
MnSO_4						
9.94	73.20	1.092	107.5	1.17	275	4.5
19.83	67.70	1.271	92.0	1.17	750	5.5
29.91	62.00	1.358	80.0	1.09	1750	5.1
40.17	55.65	1.345	73.5	0.988	5600	5.7
$\text{Mn}(m)\text{BDS}$						
9.83	73.25	1.090	89.5	0.975	9.1	5.7
19.94	67.60	1.272	76.7	.976	20	5.8
34.89	58.90	1.364	70.0	.954	85	6.3
45.73	52.15	1.296	67.2	.872	332	6.3
54.70	46.60	1.161	69.0	.801	870	5.4
65.01	40.45	0.928	73.5	.682	4400	7.2
70.17	37.30	0.827	75.0	.620	9500	6.2

data treatment were taken from the literature: densities,⁹ viscosities,¹⁰ dielectric constants.¹¹

Discussion of Results

If we compare the a_J parameter for MnSO_4 in the three solvent mixtures studied we find good agreement, with $\bar{a}_J = 5.2$ (acetone), 5.0 (dioxane), and 5.1 Å (methanol). There is no noticeable trend with solvent composition in any of the mixtures. The log K_A vs. $1/D$ plots for the three mixtures are shown in Fig. 1. The acetone-water points fall on the same line as the methanol-water points, both being distinctly higher than the dioxane-water points. This is a further example of the inadequacy of the simple Fuoss equation¹² for such salts in mixtures of polar solvents. The model for this equation ignores any deviations due

$$K_A = \left(\frac{4\pi N a^3}{3000} \right) \exp(e^2/aDkT)$$

to short-range ion solvent interactions. Further evidence for the existence of such interactions is shown in Fig. 2 where the Walden product is plotted against the dielectric constant. For both the acetone-water and methanol-water cases, a marked decrease of $\Lambda^0\eta$ occurs with increased organic component indicating a strong additional drag on the ions. This may be attributed to the ion-solvent relaxation drag recently proposed.¹³⁻¹⁵ The more ideal behavior of the Walden product in the case of the dioxane-water mixtures in the hydrodynamic analog of the thermodynamic ideality of the association constant. Both the methanol-water and acetone-water systems show the appearance of a strong ion-solvent relaxation. This makes its appearance in a lowering of the equivalent conductance at infinite dilu-

(9) "International Critical Tables," Vol. 3, p. 112.

(10) "International Critical Tables," Vol. 5, p. 22.

(11) P. S. Albright, *J. Am. Chem. Soc.*, **59**, 2098 (1937).

(12) R. M. Fuoss, *ibid.*, **80**, 5059 (1958).

(13) R. M. Fuoss, *Proc. Natl. Acad. Sci. U. S. A.*, **45**, 807 (1959).

(14) R. H. Boyd, *J. Chem. Phys.*, **36**, 1281 (1961).

(15) R. Zwanzig, *ibid.*, **38**, 1603 (1963).

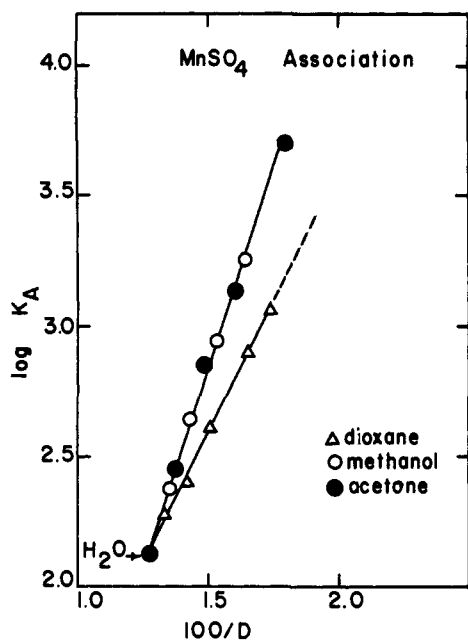


Figure 1.

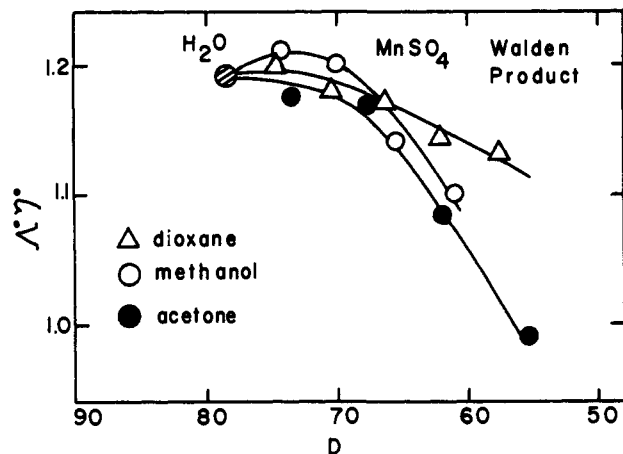


Figure 2.

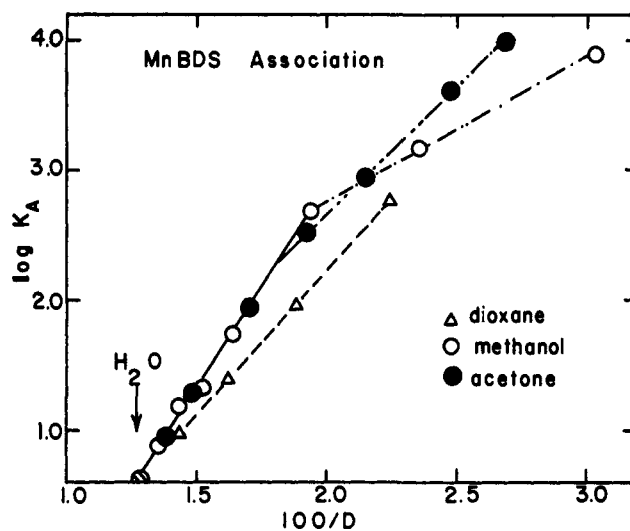


Figure 3.

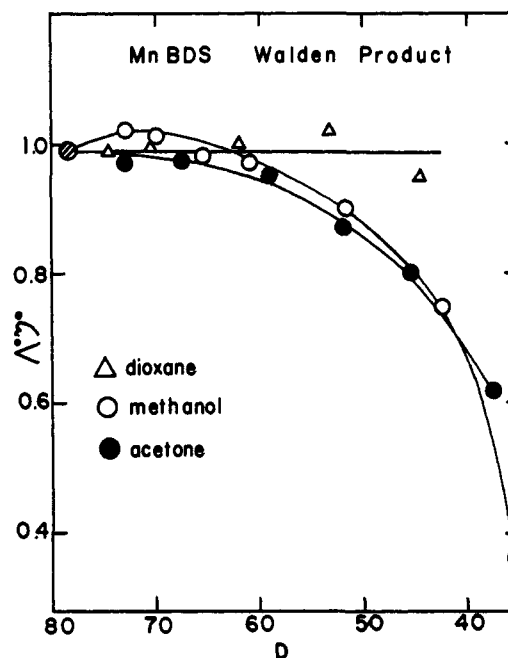


Figure 4.

tion and in an apparent dielectric constant distinctly higher than the bulk solvent value.

Very similar conclusions can be drawn from the $Mn(m)BDS$ work. Here we have the additional advantage of being able to go to higher organic concentrations. Figure 3 gives the $\log K_A$ vs. $1/D$ plot for the acetone-water mixtures together with the other two previously measured mixtures. It may be seen that up to the inflection point, the acetone-water and methanol-water mixtures can be described with the same line. Past the inflection point the behavior is quite specific to the solvent mixture and deviates less from the low organic line for the acetone than for the methanol. As in the methanol-water case, the inflection point for the acetone-water plot is coincident with the point where many of the properties of the solvent mixture exhibit maximum deviations from ideal behavior. The fact that the inflection points on the acetone-water and methanol-water plots are coincident is probably accidental. They correspond to quite different mole fractions of organic component ($X_2 = 0.25$ for methanol-water, $X_2 = 0.14$ for acetone-water). In Fig. 4 the Walden product is plotted vs. D for $MnBDS$ in the three solvent mixtures. The Walden product remains quite constant for the dioxane mixtures showing that the Stokes model furnishes an adequate description of the motion of the ions. In both of the other mixtures a

progressive lowering of $\Lambda^0 \eta$ with increasing x_2 indicates a progressively higher ion-dipole relaxation drag on the ions. The a_J parameter does not show any trend over the solvent range and the average value, 6.1 \AA. , agrees well with the dioxane-water value (6.2 \AA.) and the low organic range methanol-water value (6.0 \AA.). No evidence for a large increase of a_J in the high organic range such as was found in methanol was noted for the acetone system.

The experimental data indicate the presence of strong specific ion-solvent forces in solutions of these typical 2-2 salts. These are reflected strongly in both K_A and Λ^0 . Further analysis of this in terms of conductance terms will be deferred until the present revision¹⁶ of the conductance theory is completed. However, the authors doubt if the revised theory will make the very pronounced deviations from simple behavior noted above disappear. The revision leaves untouched any specific interactions of ions and solvent in a mixed solvent system. The problem of ion selectivity for solvent molecules in a mixture of polar solvents does not seem

(16) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **66**, 1722 (1962); **67**, 621, 628 (1963).

to be amenable to a continuum treatment but must be approached on a microscopic level.

More specifically, the data on MnSO_4 and MnBDS in dioxane-water mixtures are explained most simply by assuming that the ions are hydrated over the whole solvent composition range studied—dioxane molecules are excluded from the first coordination shells of the ions. In the case of the acetone-water and methanol-water systems, there is a competition between the water and the polar organic molecules for positions in the first coordination sphere of the ions. This competition is modified by the over-all composition of the solvent. On the water-rich side of the inflection point, the competition takes place in a water structure containing the organic polar solvent; but on the organic-rich side, it seems to occur in a quite different solvent. This is not surprising since the very strong and specific interactions between polar solvents have been known for a long time. These strong interactions must be reflected in the electrolyte properties. It must also be true that there are far more solvent systems of the methanol-water type than of the dioxane-water type. The sec-

ond type seems really to be a special case of polar solvent mixtures.

Unfortunately, conductance data alone are not sufficient to clarify this problem since we are examining second- and third-order effects. More direct evidence on such specific solvent interactions is needed. This can be provided both by conventional spectroscopic techniques and by the newer relaxation methods. In this Laboratory we are extending the conductance experiments to different solvent mixtures and examining the same systems by ultraviolet-visible and e.s.r. spectroscopy. At the same time we are using ultrasonic absorption and Wien effect dispersion measurements to probe further into the mechanism of ion association in such systems.

Acknowledgment.—The authors wish to acknowledge the support of the U. S. Atomic Energy Commission under Contract AT-(40-1)-2983 for this work. We also wish to express our thanks to Dr. Hiroyuki Tsubota for his experimental aid in the later stages of the work.

[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Molecular Complexes and Their Spectra. XVI. Complexes of Anthracene and Phenanthrene with Iodine¹

BY JANE PETERS² AND WILLIS B. PERSON³

RECEIVED MAY 31, 1963

Formation constants and molar absorptivities for complexes of iodine with anthracene and phenanthrene have been remeasured by studying the charge-transfer absorption. These complexes are extremely difficult to study quantitatively; they represent a classic example of the problems in studying weak complexes. The data were analyzed following procedures recommended by Briegleb. The value of K at 23° is 3.0 ± 0.2 for the anthracene complex and 0.45 ± 0.06 for the phenanthrene complex. The molar absorptivity for the anthracene complex at 430 $m\mu$ is about 550 ± 300 . These values of K and ϵ for the anthracene complex may still be in considerable error. It is believed that the peak of the charge-transfer band is less than 430 $m\mu$. The molar absorptivity for the phenanthrene complex at the peak of the charge-transfer band ($\lambda_{CT} = 364 m\mu$) is 7100 ± 1200 . A comparison of data for complexes of I_2 with a series of polynuclear aromatic donors indicates that the change in properties with an increasing number of rings is more gradual than reported earlier. No evidence is found for 2:1 complexes of iodine with anthracene in excess I_2 .

Introduction

Some time ago Bhattacharya and Basu reported on the charge transfer spectra of complexes between iodine and several polynuclear aromatic hydrocarbons.⁴ Since then, these measurements have achieved a special significance for several reasons. For one thing, the frequencies of the charge transfer band have been used, together with the theory, to deduce the ionization potentials of these interesting hydrocarbons. Secondly, these complexes are important as examples of complexes with a very large donor molecule and a relatively small acceptor. Murrell,⁵ for example, has used the values of intensities and formation constants to support his argument that the intensities will decrease and the formation constants will increase as the size of the donor increases. Finally we note that the base strength of these hydrocarbons has been linked with their carcinogenic activity.⁶

The values reported by Bhattacharya and Basu⁴ for the formation constant and molar absorptivity of the

phenanthrene- I_2 complex ($K = 1.06$ in units of l./mole; $\epsilon_a = 1420$ at 394 $m\mu$) differ by about a power of ten from those reported earlier by Andrews and Keefer⁷ for the same complexes ($K = 0.15$ l./mole; $\epsilon_a = 13,000$ at 396 $m\mu$). Although the value for K found by Bhattacharya and Basu agreed in order of magnitude with that found by Kortüm and Vogel in a series of solubility studies,⁸ it was thought that the importance of this complex justified reinvestigation of these measurements.

Furthermore, the unusual values of the formation constant, of the wave length of the charge transfer band, and of the molar absorptivity reported by Bhattacharya and Basu for the anthracene- I_2 complex ($K = 52$ l./mole; $\lambda_m = 430 m\mu$, and $\epsilon = 112$) suggested that the latter system should also be reinvestigated.

Briegleb⁹ has also criticized these results of Bhattacharya and Basu,⁴ pointing out that the quantity $[\text{Ar}][\text{I}_2]/D$, calculated from their data, does not vary over the concentrations of donor and iodine used in their studies. For weak complexes, at concentrations of donor and iodine such that very little complex is formed in solution, this quantity is constant and equal to $1/K\epsilon$. It is only when the concentration of donor is increased to the point that an appreciable fraction of I_2

(1) Financial support from the National Science Foundation is gratefully acknowledged.

(2) On leave 1960–1961 from Royal Holloway College, Englefield Green, Surrey, England.

(3) Guggenheim Fellow, 1960–1961. On leave from Department of Chemistry, University of Iowa, Iowa City, Iowa.

(4) R. Bhattacharya and S. Basu, *Trans. Faraday Soc.*, **54**, 1286 (1958).

(5) J. N. Murrell, *J. Am. Chem. Soc.*, **81**, 5037 (1959).

(6) A. Szent-Györgyi, I. Isenberg, and S. L. Baird, Jr., *Proc. Natl. Acad. Sci. U. S.*, **46**, 1444 (1960).

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(9) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer Verlag, Berlin, 1961, Chapter 12.