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

Solvents Having High Dielectric Constants. IV. Conductances of Ammonium and Substituted Ammonium Halides in N-Methylacetamide at 40°[1,2]

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Conductances of twenty-four ammonium and substituted ammonium halides in N-methylacetamide have been measured at 40°. In the concentration range 2–80 × 10^{-4} *N* plots of Λ *versus* $\sqrt{C}$ for all salts are linear with slopes from 2 to 23% greater than that predicted by the Onsager equation. Plots of Λ_0' *versus* *C* and of *S*Λ *versus* $Cf^2S^2\Lambda^2$ were found to be linear also for the concentration range 2–100 × 10^{-4} *N*. The results indicate that N-methylacetamide is a leveling solvent for all types of substituted ammonium halides. For a series of salts of a given type, *i.e.*, mono-substituted or di-substituted, the limiting equivalent conductance decreases with increasing weight of the alkyl group. For a series of halides, Λ_0 decreases as follows: $Me_2NH_2X > Me_3NHX > Me_4NX > MeNH_3X > NH_4X$. Dialkyl and tetraalkyl ammonium salts are more conducting than isomeric monoalkyl forms. The limiting equivalent conductance data afford numerous excellent confirmations of the Kohlrausch law of independent ion migration for solutions of electrolytes in N-methylacetamide.

An earlier paper from this Laboratory[3] describes the properties of solutions of alkali halides in N-methylacetamide. The uni-univalent salts appear to be completely dissociated in this solvent with the conductance data corresponding relatively closely to the behavior predicted by the Onsager equation up to 0.01 *M*. These results are unexpected in view of the fact that Stokes' law, upon which the Onsager equation is based, would not be expected to hold in N-methylacetamide. Positive deviations (*i.e.*, greater slopes) of the Kohlrausch plots at higher concentrations are attributed principally to viscosity effects.

It seemed of interest to study the behavior of ammonium and substituted ammonium halides in N-methylacetamide (dielectric constant = 165) to determine how the equivalent conductances of free ions in a pure solvent depend upon their nature, their concentration, the viscosity of the solvent and other factors.

Experimental

Apparatus.—Resistances were measured with a Jones bridge using alternating current in the audiofrequency range. No significant dependence of resistance upon the frequency of the impressed signal was observed. Three flask cells which have been described previously,[4] were used throughout this work. The cell constants were based upon intercomparisons of resistances of fifteen independent solutions in these cells with those of the same solutions in cells having constants which had been evaluated by the method of Jones and Bradshaw.[5] The cells were maintained at 40.00 ± 0.02° in an oil bath.

Salts.—Reagent grade ammonium halides were crystallized three times from distilled water or water–ethanol mixtures. The partially substituted ammonium bromides were synthesized by standard methods and recrystallized three times from ethanol. All other salts were obtained commercially in the best available grade and recrystallized at least twice from ethanol or ethanol–ether mixtures. Melting points of several of the salts, determined with a Fisher–Johns apparatus, showed close agreement with literature values.

Solvent.—N-Methylacetamide was purified as described previously.[3] The solvent used in this work froze above 29.5° and had the following physical properties at 40°: conductivity, 0.7–2.0 × 10^{-7} ohm^{-1} cm.$^{-1}$; density, 0.9420 g./ml.; viscosity, 0.03020 poise; dielectric constant, 165.5 (at 10 megacycles).

Solutions.—All solutions were prepared on a weight basis with transfers made in a dry box under a positive pressure of nitrogen. Friedman–LaMer weighing pipets were used for making successive additions of approximately 0.02 *N* stock solution to the solvent contained in a conductance cell. All weights were corrected to vacuum. The conductivity of a salt was obtained by subtracting the conductivity of the solvent from that of the solution. The maximum solvent correction usually did not exceed 3% of the total conductance.

Results

Available space does not permit tabulation of corresponding values of the equivalent conductance and the concentration for each of the twenty-four salts.[6] Trends in the data are presented graphically and the results are summarized in Tables I, II and III.

Discussion

The solute concentration ranged from 2 × 10^{-4} to 8 × 10^{-3} *N* or greater except for the sparingly soluble tetramethylammonium iodide for which the upper limit was 10 × 10^{-4} *N*. Figure 1 shows plots of the equivalent conductance of several of the ammonium and substituted ammonium salts in N-methylacetamide as a function of the square root of the concentration. The radii of the circles representing the experimental data are equivalent to 0.06 Λ unit or approximately 0.25% of the ordinate value which corresponds to the estimated total experimental error. The open and solid circles represent data obtained from independent series of solutions for each salt. A linear Kohlrausch plot was obtained for each salt for the concentration range 2–80 × 10^{-4} *N*. From Fig. 1, it is evident that the experimental data show close agreement with the Onsager slope (represented by a dashed line) especially for the more dilute solutions. In most cases at concentrations greater than 80 × 10^{-4} *N*, the plots begin to turn downward. Table I contains values of the limiting equivalent conductances which were obtained by mathematical extrapolations of the plots of Λ *versus* $\sqrt{C}$ and also comparisons of the experimental and theoretical slopes. In every case the experimental slope was found to be

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(1) Presented at the 128th Meeting of the American Chemical Society in Minneapolis, September, 1955.

(2) This work was supported in part by a contract with the Office of Ordnance Research.

(3) L. R. Dawson, P. G. Sears and R. H. Graves, THIS JOURNAL, **77**, 1986 (1955).

(4) D. P. Ames and P. G. Sears, *J. Phys. Chem.*, **59**, 16 (1955).

(5) G. Jones and B. C. Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

(6) Tables of equivalent conductance and concentration data have been deposited as Document number 4751 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

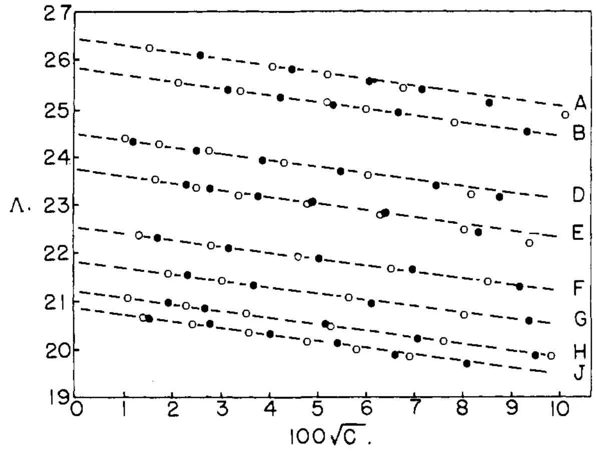

Fig. 1.—Kohlrausch plots for typical salts in N-methylacetamide at 40°: A, Me_2NH_2Br; B, Me_3NHBr; D, Et_4NBr; E, Pr_4NBr; F, NH_4Br; G, Me_3PhNCl; H, NH_4Cl; J, Bu_2NH_2Cl. Dashed lines represent Onsager slopes.

numerically greater than the Onsager slope; the differences ranged from 2 to 23% with a mean of 11%. In general, better agreement between the slopes was found for the alkali metal salts[3] and ammonium salts than for the quaternary ammonium salts.

TABLE I

TEST OF ONSAGER'S EQUATION FOR SOLUTIONS OF SALTS IN N-METHYLACETAMIDE AT 40°

Salt	Λ_0	Expt. slope (S_E)	Theor. slope (S_T)	$\frac{S_E - S_T}{S_T}100$
NH_4I	24.30	14.1	13.7	4
NH_4Br	22.50	14.0	13.6	3
NH_4Cl	21.18	13.7	13.5	2
Me_4NI	26.65	16.3	13.8	18
Me_4NBr	24.80	15.3	13.7	12
Me_4NCl	23.58	14.3	13.6	5
Et_4NI	26.25	16.7	13.8	21
Et_4NBr	24.50	15.5	13.7	13
Pr_4NI	23.74	16.7	13.6	23
Pr_4NBr	22.01	15.9	13.5	18
Bu_4NI	22.35	16.0	13.6	18
Me_3PhNI	24.80	15.7	13.7	15
Me_3PhNCl	21.80	14.0	13.5	4
$MeNH_3Cl$	23.43	15.4	13.6	13
Me_2NH_2Cl	25.23	15.2	13.7	11
Me_3NHCl	24.40	16.5	13.7	20
$MeNH_3Br$	24.73	14.4	13.7	5
Me_2NH_2Br	26.46	15.6	13.8	13
Me_3NHBr	25.72	14.0	13.8	2
$EtNH_3Cl$	22.39	15.6	13.6	11
$EtNH_3Br$	23.71	14.6	13.6	7
Et_2NH_2Cl	23.47	15.6	13.6	15
$BuNH_3Cl$	21.33	15.8	13.5	10
Bu_2NH_2Cl	20.90	14.8	13.5	10

It may be noted also from Table I that the theoretical slope of the plot for every salt lies between 13.5 and 13.8. This nearly constant value results primarily from the fact that approximately 85% of the theoretical slope is accounted for by the electrophoretic effect which is the same for each salt and is independent of the magnitude of Λ_0.

Conductance data for a few typical salts were analyzed by the Shedlovsky extrapolation equation.[7] Values of the limiting equivalent conductances agreed very closely with corresponding values obtained by other methods; however, "dissociation constants" calculated from the slopes of the plots of $S\Lambda$ *versus* $Cf^2S^2\Lambda^2$ were very large (greater than 0.2) and were considered to have little, if any, significance other than indicating that the dissociation of the salts in N-methylacetamide is quite complete even at appreciable concentrations.

The Shedlovsky rearrangement of the Onsager equation[8] is particularly useful for calculating the limiting equivalent conductances of salts in N-methylacetamide directly from Λ values. Limiting equivalent conductances calculated in this manner are designated by Λ_0' and generally are found to deviate from the true limiting equivalent conductance, Λ_0, by a linear function of the concentration as

$$\Lambda_0' = \frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} = \Lambda_0 + BC \qquad (1)$$

which for salts in N-methylacetamide at 40° becomes

$$\Lambda_0' = \frac{\Lambda + 11.99\sqrt{C}}{1 - 0.0695\sqrt{C}} = \Lambda_0 + BC \qquad (2)$$

If equation 2 applies, a linear plot of Λ_0' *versus* C should yield an intercept of Λ_0 and have a slope of B. Figure 2 shows several typical plots for salts in N-methylacetamide. A linear plot with a small negative slope was obtained for each salt for the concentration range 2–100 × 10^{-4} N. Pertinent data for each salt obtained by mathematical extrapolations of plots of equation 2 are presented in Table II. Corresponding values of Λ_0 in Tables I and II in some cases differ by a few hundredths of a unit; however, it is believed that those in Table II are probably more accurate inasmuch as a better extrapolation procedure was used.

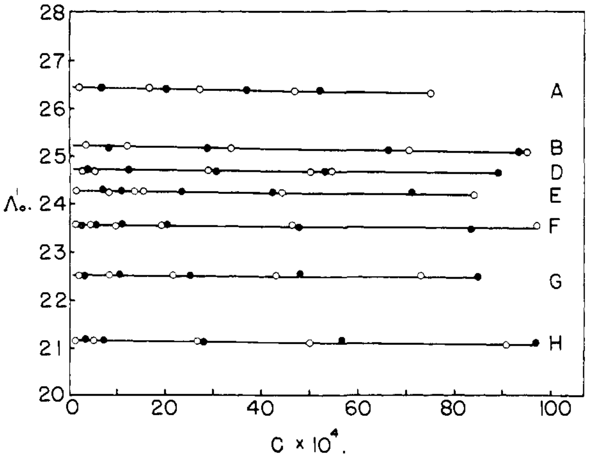

Fig. 2.—Plots of equation 2 for typical salts in N-methylacetamide at 40°: A, Me_2NH_2Br; B, Me_2NH_2Cl; D, Me_4NBr; E, NH_4I; F, Me_4NCl; G, NH_4Br; H, NH_4Cl.

The small negative slope in each case may be the result of a change of viscosity with concentration. In a previous investigation[3] it was found that the viscosity of a 0.01 N solution of a uni-univalent salt in N-methylacetamide is approximately 1%

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[7] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

[8] T. Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

TABLE II

DATA DERIVED FROM PLOTS OF THE SHEDLOVSKY MODIFICATION OF THE ONSAGER EQUATION

Salt	Λ_0	B	Salt	Λ_0	B
NH_4I	24.27	− 7	Me_3PhNCl	21.80	−15
NH_4Br	22.52	− 5	$MeNH_3Cl$	23.43	−18
NH_4Cl	21.18	− 4	Me_2NH_2Cl	25.22	−18
Me_4NI	26.66	−35	Me_3NHCl	24.40	−25
Me_4NBr	24.79	−11	$MeNH_3Br$	24.69	−11
Me_4NCl	23.58	− 8	Me_2NH_2Br	26.44	−15
Et_4NI	26.21	−37	Me_3NHBr	25.72	− 4
Et_4NBr	24.47	−11	$EtNH_3Cl$	22.38	−22
Pr_4NI	23.73	−31	$EtNH_3Br$	23.72	−16
Pr_4NBr	22.01	−31	Et_2NH_2Cl	23.45	−27
Bu_4NI	22.34	−39	$BuNH_3Cl$	21.33	−23
Me_3PhNI	24.80	−18	Bu_2NH_2Cl	20.89	−26

greater than that of the pure solvent. If the experimental Λ values were multiplied by the relative viscosity of the solution, corrected plots of Λ_0' *versus* C would exhibit positive rather than negative slopes; also plots of Λ *versus* $\sqrt{C}$ would exhibit slopes which would be approximately 10% (numerically) less rather than 10% greater than the Onsager slopes.

Differences of the limiting equivalent conductances of salts having a common cation may be found in Table III. If the estimated maximum uncertainty in any Λ_0 value is 0.06 unit, a difference based upon two Λ_0 values should have a possible inherent uncertainty of 0.12 unit. The values in Table III indicate the maximum deviation from a mean difference in anionic conductances in no case exceeds 0.09 unit, which testifies to the general consistency of the results.

TABLE III

DIFFERENCES IN LIMITING EQUIVALENT CONDUCTANCES OF HALIDES HAVING COMMON CATIONS IN N-METHYLACETAMIDE AT 40°

	$(I^- - Br^-)$		$(Br^- - Cl^-)$		$(I^- - Cl^-)$
NH_4^+	1.75	NH_4^+	1.34	NH_4^+	3.09
Me_4N^+	1.87	Me_4N^+	1.21	Me_4N^+	3.08
Et_4N^+	1.74	$MeNH_3^+$	1.26	Me_3PhN^+	3.00
Pr_4N^+	1.72	$Me_2NH_2^+$	1.22		
		Me_3NH^+	1.32		
		$EtNH_3^+$	1.34		

Assuming that any cationic conductance is independent of the particular anion present, the following series of sixteen increasing relative cationic conductances can be deduced from the data presented in Table II and in an earlier paper[3]

$$Li^+ < Bu_4N^+ < Na^+ < K^+ < Pr_4N^+ < Bu_2NH_2^+ < NH_4^+ < BuNH_3^+ < Me_3PhN^+ < EtNH_3^+ < Et_4N^+ < MeNH_3^+ < Et_2NH_2^+ < Me_4N^+ < Me_3NH^+ < Me_2NH_2^+$$

If the position of the alkali metal ions in this series is interpreted to mean that their effective sizes approximate those of the Pr_4N^+ and Bu_4N^+ ions, they must be solvated. It is difficult to believe, however, that each ion could be surrounded by a sheath of molecules in N-methylacetamide where a chain-like molecular structure predominates. It seems more likely that "solvation" here consists of ion–solvent interaction without the attachment of specific solvent molecules to an ion. Such interaction would produce distortion of the quasicrystalline structure of the solvent and would interfere with the motion of the ions under an applied electrical potential. This effect would be expected to be relatively large for the alkali metal ions because of their higher charge density. It is interesting to note that the sodium and potassium ions are less conducting than the Pr_4N^+ ion in N-methylacetamide whereas the latter ion is less conducting in the isomeric solvent dimethylformamide.[9] Assuming that the Pr_4N^+ ion is unsolvated in both media, this would imply that the alkali metal ions are relatively more solvated in N-methylacetamide in contrast to the expectation that these cations would be solvated to a greater extent in the more basic dimethylformamide. The explanation must lie in the differences in the molecular constitution of the solvents.

N-Methylacetamide, like water, acts as a leveling medium producing complete dissociation of all substituted ammonium salts. These salts, however, display extremely unusual behavior insofar as their limiting equivalent conductances are related to the degree of substitution. Plots of the limiting equivalent conductance as a function of the degree of substitution for series of methylammonium bromides and chlorides are shown in Fig. 3. Parallelism of the plots results from independent ion migration effects, but the fact that the maximum Λ_0 value is displayed by the di-substituted salt is quite unexpected. This behavior constitutes pronounced departure from the pattern of behavior usually observed in which Λ_0 decreases steadily with increasing extent of substitution. These results lead to the conclusion that stronger solute–solvent interaction exists with the ammonium and methylammonium ions. In addition to ion–dipole attraction, there is also the possibility of cation–solvent interaction through hydrogen bonding.

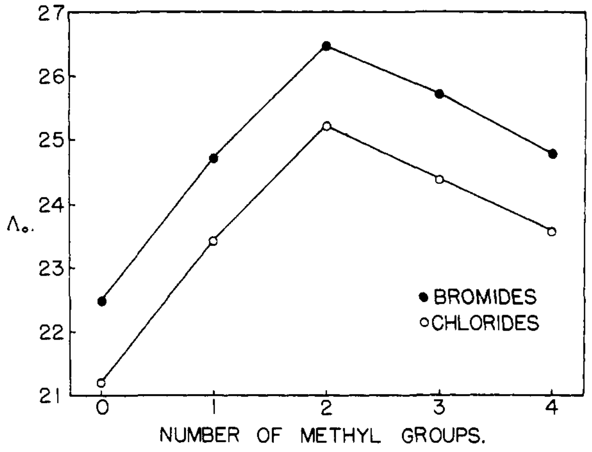

Fig. 3.—Limiting equivalent conductances of methylammonium halides.

Figure 4 shows the limiting equivalent conductance as a function of the nature of several substituted ammonium chlorides. The conductances of the tetraethylammonium and tetra-*n*-butylammonium chlorides have been calculated from the data

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[9] P. G. Sears, E. D. Wilhoit and L. R. Dawson, *J. Phys. Chem.*, **59**, 373 (1955).

for the iodides in Tables II and III. Whereas the dimethylammonium and diethylammonium salts display the maximum limiting equivalent conductances in the methyl and ethyl series, the monobutylammonium salt is most conducting in the butyl series.

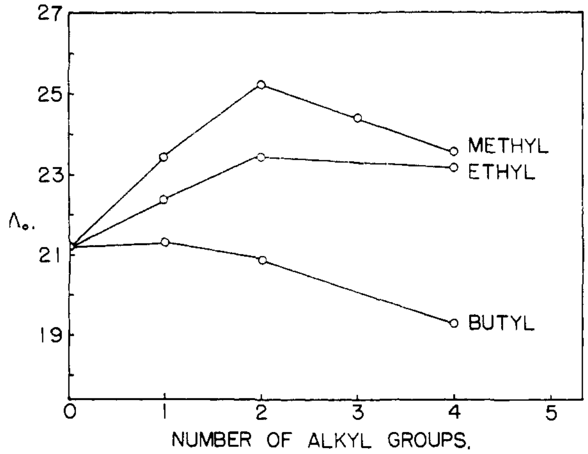

Fig. 4.—Limiting equivalent conductances of substituted ammonium chlorides.

Other aspects of the conductance behavior of the substituted ammonium salts are normal. For isomeric cations, the relative conductances increase with increasing symmetry of the cation as shown by the following examples

$$BuNH_3^+ < Et_2NH_2^+ < Me_4N^+$$
$$Bu_2NH_2^+ < Et_4N^+$$
$$EtNH_3^+ < Me_2NH_2^+$$

For similarly substituted cations, the conductances increase with decreasing formula weight of the cation

$$BuNH_3^+ < EtNH_3^+ < MeNH_3^+$$
$$Bu_2NH_2^+ < Et_2NH_2^+ < Me_2NH_2^+$$
$$Bu_4N^+ < Pr_4N^+ < Me_3PhN^+ < Et_4N^+ < Me_4N^+$$

The following series of decreasing relative conductances of the symmetrically substituted quaternary ammonium ions shows that the difference (in Λ units) between the conductances of the Me_4N^+ and Et_4N^+ ions is very small in comparison to those for the other two cases.

$$Me_4N^+ \overset{0.35}{>} Et_4N^+ \overset{2.50}{>} Pr_4N^+ \overset{1.39}{>} Bu_4N^+$$

Similar results for the same series of cationic conductances in nitrobenzene have been reported by Taylor and Kraus[10] who postulated that the greater charge density on the Me_4N^+ ion causes appreciable ion–dipole interaction resulting in additional retardation of the mobility of that ion.

[10] E. G. Taylor and C. A. Kraus, This Journal, **69**, 1731 (1947).

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[Contribution from the Department of Chemistry, University of Utah]

The Mass Spectra of Four Deuterated Butanes

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The mass spectra of *n*-butane-2-*d*, *n*-butane-1,1,1-d_3, *n*-butane-1,1,1,3,3-d_5 and *n*-butane-1,1,1,2,2,3,3-d_7 using 80 volt electrons at 100° are compared with that of *n*-butane. The results are discussed with respect to the isotope effect, rearrangement phenomena, and activated complexes. The rate of H–D exchange in the parent molecule–ions is slower than the rate of C–C bond break, but faster than the rate of loss of H_2 or HD. Such exchange occurs between atoms on adjacent carbons and on carbons 1–3 and 1–4.

I. Introduction

A theory of mass spectra of polyatomic molecules, with reference primarily to saturated hydrocarbons, has been presented.[3–5] The mass spectra are assumed to arise from the quasi-equilibrium decomposition of the parent molecule–ion through a sequence of competing unimolecular reactions. Using thermal data combined with mass spectral appearance potentials, Wahrhaftig and co-workers obtained a set of reactions and activation energies for the decomposition of propane. The detailed application of these permitted the satisfactory calculation of the major aspects of the mass spectra of propane and propane-2,2-d_2, including the metastable transition peaks of propane.[6] However, on attempting to make similar calculations for butane and isobutane, it was found that more information was needed on the reaction scheme than could be obtained from a study of the mass spectra of the normal compounds. In order to gain further information on the rearrangements preceding and accompanying the decomposition reactions, three new deuterated butanes have been prepared and studied.

II. Experimental

Apparatus.—All mass spectra reported in this paper were obtained on a mass spectrometer constructed at the University of Utah. This machine is of the usual sector field type developed by Nier, with 90° deflection at an 8 inch radius. The details of operation were as follows.

Background pressure in the main tube was between 2.5 × 10^{-6} and 4.5 × 10^{-6} mm. The gas samples were stored at 20 mm. pressure and were introduced into the ionization region at the rate of approximately 0.5 cc./min. An electron accelerating potential of 80 volts was used in all runs. Total electron emission was in the range of 35–60 micro-

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[1] From a dissertation in partial fulfillment of the requirements for the Ph.D. degree, University of Utah, 1954. Now at the Department of Chemistry, Cornell University.

[2] The construction of the mass spectrometer used in this research was initiated under a grant from the University of Utah Research Fund. This research was assisted by the U. S. Atomic Energy Commission under Contract AT(11-1)-82, Project No. 5.

[3] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig and Henry Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952).

[4] M. B. Wallenstein, Ph.D. Thesis, University of Utah, 1951.

[5] H. M. Rosenstock, Ph.D. Thesis, University of Utah, 1952.

[6] Allen Kropf, Ph.D. Thesis, University of Utah, 1954.