Procedure

A neutral solution containing 312 g. of mixed rare earths weighed as oxide, was obtained by dissolving a known larger amount of the rare earth material in a limited amount of hydrochloric acid and recovering the undissolved rare earth. A previously prepared solution of diammonium dihydrogen versenate, containing the theoretical amount of Versene required to complex the heavy rare earths in the mixture, and adjusted to a *p*H of 10, was then added to the rare earth solution, and the combined solution diluted to 90 liters. After equilibrating for 24 hours, the *p*H of the solution was adjusted to 4.5 with a little hydrochloric acid. Following a second 24-hour equilibration period, this solution was passed rapidly through a short bed of Dowex-50, and the column washed free of complexed rare earths with a few liters of distilled water. The rare earth material remaining on the resin was removed fractionally by pouring four successive predetermined amounts of Versene solution, which had been adjusted to a *p*H of 9.5, through the column at a slow flow rate, taking 24 hours for each fraction, so as to let the liquid remain in contact with the resin long enough to approach equilibrium conditions.

Results and Discussion

To obtain an analysis of the five fractions, 20 g. of oxide from each fraction was adsorbed on standard, small ion-exchange columns and eluted with citric acid according to our usual procedure for obtaining pure rare earths. This spread the fractions out into 20 to 30 secondary fractions, each of which contained only two to four rare earths. These secondary fractions could then be analyzed spectrographically and spectrophotometrically without running into the interferences which would occur in a direct analysis of the larger fractions. Also, much better material balances could be obtained. The results are presented in Table I.

TABLE I

RARE EARTH OXIDES RECOVERED IN ONE RUN ON GADOLINITE ORE (GRAMS)

Elements	Sample I	Sample II	Sample III	Sample IV	Sample V	Total
Lu	1.67	...	...	...	...	1.67
Yb	14.02	1.69	...	...	...	15.71
Tm	1.55	1.22	...	...	...	2.77
Er	5.58	9.83	...	...	...	15.41
Ho	1.04	3.57	0.25	...	...	4.86
Dy	2.15	11.17	9.04	0.30	...	22.66
Tb	0.06	0.13	0.10	0.75	0.69	1.73
Gd	...	...	...	7.37	5.80	13.17
Sm	...	...	...	3.87	5.42	9.29
Nd	...	...	...	3.75	7.45	11.20
Pr	...	...	...	0.37	0.68	1.05
Ce	...	...	...	.81	2.27	3.08
La	...	...	...	.81	2.27	3.08
Y	13.81	65.17	72.80	25.80	13.22	190.80
Total	39.88	92.78	82.19	43.83	37.80	296.48

It will be noticed that under these very preliminary conditions, which are almost certainly far from optimum, most of the heavy rare earths are concentrated away from the light rare earths and from most of the yttrium. Such a preliminary separation will permit us to add five times as much heavy rare earths on the ion-exchange columns as we could previously and therefore step up our production of these pure rare earths accordingly.

At the present time, we are studying the possibility of greatly improving this process by investigating such variables as a higher temperature to approach the various equilibria more rapidly, and utilizing more concentrated solutions to increase the yields.

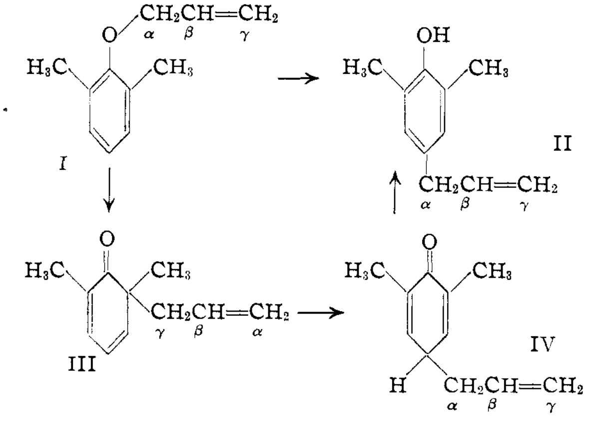
CONTRIBUTION NO. 212 FROM THE INSTITUTE FOR
ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY
AMES LABORATORY OF THE ATOMIC ENERGY COMMISSION
IOWA STATE COLLEGE, AMES, IOWA

COMMUNICATIONS TO THE EDITOR

THE MECHANISM OF THE *PARA*-CLAISEN REARRANGEMENT

Sir:

Consideration of the literature[1-6] dealing with the *para*-Claisen rearrangement, of which the change I → II is an example, led us to suspect the intermediate formation of isomeric cyclohexadienones, *e.g.*, III and IV. Since III is a type which should readily participate in Diels–Alder additions, it was hoped that this substance, if present in the reaction mixture, might be trapped when the rearrangement was conducted in the presence of some suitable dienophile.



Allyl 2,6-dimethylphenyl ether, in a solution of maleic anhydride, was heated (200° for 2.5 hours, CO_2 atm.) and the acidic reaction products separated. One of these, m.p. 143 3–143.6°, obtained

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(1) O. Mumm, *et al.*, *Ber.*, **70**, 2214 (1937); **72**, 100 (1939); **72**, 1523 (1939).

(2) D. S. Tarbell and J. F. Kincaid, THIS JOURNAL, **62**, 728 (1940).

(3) C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939).

(4) E. R. Alexander and R. W. Kluiber, THIS JOURNAL, **73**, 4304 (1951).

(5) D. S. Tarbell, chapter in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 1.

(6) H. B. Watson, *Ann. Repts. Chem. Soc.*, 206 (1939).

in 6.3% yield, is evidently one of the possible stereoisomeric Diels-Alder adducts of III, from the following data: calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.30; H, 6.31. Infrared: 5.42, 5.63 μ (cyclic 5-ring anhydride) and 5.83 μ (6-ring saturated ketone). Ultraviolet: No high intensity maxima; λ_{max} 300 mμ, $\epsilon = 64$. The adduct was slowly soluble in sodium hydroxide solution, decolorized permanganate rapidly, and was converted after the uptake of exactly two molar equivalents of hydrogen (Pt catalyst) to a tetrahydro derivative, m.p. 115.1–115.4° (calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.15; H, 7.74.) which was saturated to permanganate, and gave an infrared spectrum whose carbonyl region was substantially identical with that of the adduct.

The phenol (II) gave no trace of adduct under identical conditions, with an identical isolation procedure. The ether (I) gave no trace of adduct with maleic anhydride at 100° for three hours. However the pure ether, when heated alone at 200° for ten minutes, produced a mixture actually containing some dienone, since a small amount of the adduct could be isolated after treatment of the mixture with maleic anhydride at 100° for three hours. Finally, pyrolysis of the pure adduct in Nujol solution (200° for 3.75 hours) yielded phenol (II), isolated as the phenylurethan, m.p. 141.5–143°, identical with an authentic sample,[2] in 2% over-all yield. Evidently the dienone (III), when released from its adduct, can rearrange further to the final product (II).

The data require that I → III → (IV) → II is a reaction path actually used, if not the sole reaction path. In analogy to the *ortho* Claisen rearrangement, the dienone (III) is presumably formed from I through a six-membered transition state in which the bonds are made and broken simultaneously.[1,6] But unlike the enolizable dienone formed in the *ortho* rearrangement, III can return to an aromatic system only by an additional longitudinal flip of the allyl group, to give IV, which then enolizes to II. In a sense, the change III → IV is comparable to the thermal transformation of ethyl 1-cyclohexenylallylcyanoacetate to ethyl (2-allylcyclohexylidene)-cyanoacetate,[7] an all-carbon allylic rearrangement.

This mechanism for the *para*-Claisen rearrangement predicts no α-γ inversion of the allyl group in the over-all process, a result borne out by several previous experiments,[1,8] is consistent with the finding that an optically active allyl residue retains activity in *para* migration[4], and is in agreement with the fact[2] that both *ortho* and *para* rearrangements have comparable entropies of activation.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY HAROLD CONROY[9]
NEW YORK 27, N. Y. RAYMOND A. FIRESTONE

RECEIVED NOVEMBER 24, 1952

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[7] A. C. Cope, *et al.*, THIS JOURNAL, **62**, 441 (1940); **63**, 1843 (1941); **63**, 1852 (1941).

[8] NOTE ADDED APRIL 30, 1953.—Although some of the experiments of Mumm, *et al.* (ref. 1), seemed inconsistent with this view, these have very recently been repeated (S. J. Rhoads, R. Raulins and R. D. Reynolds, THIS JOURNAL, **75**, 2531 (1953)) and the difficulty resolved. *Cf.* also J. P. Ryan and P. R. O'Connor, *ibid.*, **74**, 5866 (1952), who demonstrated the point with *labelled* compounds.

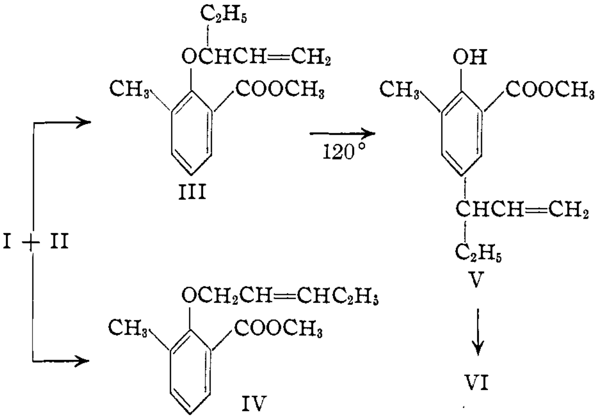
[9] Process Research, Merck & Co., Inc., Rahway, N. J.

ON THE *PARA*-CLAISEN REARRANGEMENT

Sir:

Renewed interest in the *para*-Claisen rearrangement[1,2] prompts us to report our findings on reinvestigation of the work of Mumm, Hornhardt and Diederichsen[3] on the preparation and rearrangement of the α- and γ-ethylallyl ethers of methyl cresotinate, III and IV. Contrary to the conclusions reached by the earlier workers, we have obtained evidence that the *para*-rearrangement proceeds *without inversion* of the migrating group in both III and IV.

The reaction of sodio-methyl cresotinate, I, with α-ethylallyl chloride, II, in methanol gives rise to a mixture of III and IV as well as a phenolic fraction containing both possible C-allylated phenols. The separation of the neutral and phenolic fractions *cannot* be accomplished with 2 *N* sodium hydroxide (*cf.* ref. 3) but requires the use of Claisen alkali.



Vacuum distillation of the ethereal fraction gives material with a negative ferric chloride test, b.p. 92–116° at 0.2 mm., $n^{25}D$ 1.5072–1.5119. Methanolic potassium hydroxide hydrolysis of the higher boiling end fraction of this material yields the acid corresponding to the γ-ether, IV, m.p. 63.5–64°, identical by mixed m.p. with an authentic sample. Hydrolysis of the lower boiling end fraction of the ethereal material proceeds *without rearrangement* (*cf.* ref. 3) furnishing an oil which crystallizes at −5° but remelts at room temperature. Ozonolysis of the ethereal fraction produces formaldehyde in amounts corresponding to 40 ± 5% of an ether with a terminal methylene group. Ozonolysis of the same ethereal material, followed by hydrogen peroxide-acetic acid oxidation permits the isolation of 2-carboxy-6-methylphenoxyacetic acid (20–30%), identical with that produced by the oxidation of pure IV. Comparision of the infrared spectra of the ethereal fraction, authentic γ-ether and a model compound, the allyl ether of methyl cresotinate, confirms the presence of IV in the α-ether preparation, but the characteristic 10.7–10.8μ peak of the terminal methylene group is also detectable.

Separation of III and IV by fractional distillation is precluded by the thermal sensitivity of the

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[1] J. P. Ryan and P. R. O'Connor, THIS JOURNAL, **74**, 5866 (1952).

[2] H. Schmid and K. Schmid, *Helv. Chim. Acta*, **35**, 1879 (1952).

[3] O. Mumm, H. Hornhardt and J. Diederichsen, *Ber.*, **72**, 100 (1939); O. Mumm and J. Diederichsen, *ibid.*, **72**, 1523 (1939).

ethers. A preferential rearrangement of the α-ether III has proved feasible, however. When held at 120° for 18 hours III undergoes rearrangement with the appearance of a deep blue ferric chloride test; a sample of pure IV, under the same conditions, develops only a very faint ferric chloride test. Claisen alkali extraction of the preferentially rearranged α-ether preparation permits the isolation of relatively pure rearranged α-ether, V, b.p. 95–96° at 0.18 mm; n^{20}_{D} 1.5266. Hydrolysis of V yields an acid, VI, m.p. 102.5–103°, *not identical* with the corresponding acid from the rearranged γ-ether, m.p. 115–116°[3], mixed m.p. 72–94°. *Anal.* of VI, calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.33; Found, C, 70.68; H, 7.58. Ozonolysis of V produces formaldehyde in amounts corresponding to 84 ± 8% rearrangement product with a terminal methylene group. Infrared spectra likewise confirm the terminal methylene group of V.

The generally accepted idea concerning the course of the *para*-Claisen rearrangement, *i.e.*, that the rearrangement proceeds in a way that allows equilibration of the migrating allylic system,[4,5,6] appears, therefore, erroneous; instead the rearrangement proceeds without inversion and must involve partial bonding of a sort which maintains, or restores, the original structure of the migrating fragment. Our findings accord with the results of Ryan and O'Connor[1] and with observations made by Marvell on a comparable pair of ethers.[7]

This work received support from the Research Corporation and the American Academy of Arts and Sciences.

[4] D. S. Tarbell, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 3.

[5] G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 548.

[6] P. D. Bartlett, "Organic Chemistry, an Advanced Treatise," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 72.

[7] Dr. E. N. Marvell, private communication.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WYOMING
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SARA JANE RHOADS
REBECCA RAULINS
ROSALIE D. REYNOLDS

RECEIVED APRIL 18, 1953

ISOLATION AND CHARACTERIZATION OF GLYCOPROTEINS FROM HUMAN PLASMA

Sir:

Human plasma contains several glycoproteins which are distinguished by their acid isoelectric points and their low molecular weights. Recently, the major component of these glycoproteins (the "acid glycoprotein," an α_1-globulin) has been described.[1,2]

The purpose of this note is to report the isolation from human plasma of a further group of such glycoproteins and to describe some of their properties.

The starting material for these studies was the supernatant solution of Fraction V obtained after precipitation of over 98% of the proteins from pooled normal human plasma, according to the low temperature–low salt–ethanol fractionation method.[3] The proteins (Fraction VI) in this supernatant solution were concentrated with the aid of zinc hydroxide and fractionated by a method described earlier.[2] Following removal of the proteins identical with those of Fraction V and of the acid glycoprotein from Fraction VI, the remaining protein fraction appeared essentially homogeneous in the ultracentrifuge ($S_{20,w}$ approximately 3) and by electrophoresis at *p*H 8.6. The electrophoretic mobility, $u = -4.2 \times 10^{-5}$ cm.^{2}/volt × sec., corresponded to an α_2-globulin.

In acetate buffer solutions of ionic strength 0.1, this α_2-protein fraction separated into three components. Taking advantage of the specific interaction with cations, these α_2-glycoproteins were fractionated from each other. Two proteins were rendered insoluble, at low ionic strength, *p*H 5.7 and at −5°, in a solution containing 19% ethanol by addition of barium acetate to give a final concentration of 0.02 *M*. Further addition of an equal amount of zinc acetate to the supernatant solution precipitated the third glycoprotein[4] which was isoelectric between *p*H 4.1 and 4.3. The optical density in a 1-cm. cuvette of a 1% solution ($E^{1\%}_{1\text{ cm.}}$) of the latter protein was approximately 15 at 278 mμ. The "barium-insoluble" proteins were separated from each other under similar conditions. After exchange of the protein-bound barium ions for zinc ions, one of these plasma constituents was removed as insoluble zinc-lead-complex upon the addition of lead acetate. This "lead-insoluble" glycoprotein, showing an extinction coefficient of approximately 5 at 278 mμ, was denatured in acid phosphate buffer solutions as judged by the insolubility in 0.15 *M* NaCl solution. Its isoelectric point was found to be between *p*H 3.5 and 3.8. The protein which remained in solution and represented the major component of these α_2-glycoproteins, absorbed at 278 mμ with a coefficient ($E^{1\%}_{1\text{ cm.}}$) of about 5. Its isoelectric point was near *p*H 4.

Further details of these investigations will be reported later.

The author wishes to thank Dr. J. A. McComb, director of the Division of Biologic Laboratories, Massachusetts Department of Health, for providing the starting material.

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[1] H. E. Weimer, J. W. Mehl and R. J. Winzler, *J. Biol. Chem.*, **185**, 561 (1950).

[2] K. Schmid, THIS JOURNAL, **75**, 60 (1953).

[3] E. J. Cohn, L. E. Strong, W. L. Hughes, Jr., D. J. Mulford, J. N. Ashworth, M. Melin and H. L. Taylor, *ibid.*, **68**, 459 (1946).

[4] This was the only glycoprotein which was colored.

THE ROBERT W. LOVETT MEMORIAL FOUNDATION
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RECEIVED APRIL 18, 1953

THE REARRANGEMENT OF THE NEOPHYL RADICAL

Sir:

Although several examples of the migration of a phenyl group to an adjacent radical center have been published,[1] no evidence concerning the process by which this rearrangement takes place has been reported. It has now been found that, in contrast to similar ionic migrations which pro-

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[1] (a) W. H. Urry and M. S. Kharasch, THIS JOURNAL, **66**, 1438 (1944); (b) S. Winstein and F. H. Seubold, Jr., *ibid.*, **69**, 2916 (1947); (c) W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952); (d) D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952).

ceed through a cyclic "phenonium ion,"[2] the neophyl (β-phenylisobutyl) radical is produced as a discrete entity which may either interact with the solvent to yield unrearranged product, in the present case *t*-butylbenzene, or undergo isomerization to the β-phenyl-*t*-butyl radical by a 1,2-phenyl shift with an activation energy of approximately 8 kcal./mole to yield isobutylbenzene. As in previous investigations, no migration of the methyl group was observed.

The di-*t*-butyl peroxide-catalyzed decomposition of β-phenylisovaleraldehyde[1b] was carried out at 130° with the pure liquid aldehyde (initially 6.4 molar) and with a 1.0 molar solution of the aldehyde in chlorobenzene, a solvent known to be relatively inert to free radical attack.[3] The butylbenzene fractions, obtained in yields of 71 and 57% in the two reactions, respectively, were separated first by steam distillation and then analyzed by fractionation through a Piros–Glover spinning-band column at a 100:1 reflux ratio, by refractive index of the fractions, and by comparison of the infrared spectra with known standards.

If a cyclic intermediate which could react at either of two sites with the solvent to yield the observed products were important, the ratio isobutylbenzene (R_2H)/*t*-butylbenzene (R_1H) should be independent of the concentration of the hydrogen atom donor, in this case the aldehyde. The observed ratio, however, increased from 1.3 to 4.0 as the aldehyde concentration was decreased. This result is in accord with the reaction sequence

$$\begin{gathered} R_1\dot{C}O \xrightarrow{k_1} R_1\cdot + CO \\ R_1\cdot + R_1CHO \xrightarrow{k_2} R_1H + R_1\dot{C}O \\ R_1\cdot \xrightarrow{k_3} R_2\cdot \\ R_2\cdot + R_1CHO \xrightarrow{k_4} R_2H + R_1\dot{C}O \\ \frac{(R_2H)}{(R_1H)} \approx \frac{d(R_2H)}{d(R_1H)} = \frac{k_3}{k_2(R_1CHO)}\,. \end{gathered}$$

This mechanism is strengthened by the observation that the peroxide-catalyzed chlorination of *t*-butylbenzene yields only the unrearranged derivative,[5] attack of the neophyl radical on such a highly reactive substrate as chlorine being so rapid as to preclude rearrangement.

The decomposition of the pure aldehyde was carried out at 150°, 57 ± 3% rearrangement, and at 170°, 63 ± 3% rearrangement, as well as at 130°, 57 ± 3% rearrangement. This small change over a 40° interval indicates that the activation energy for migration of a phenyl group to an adjacent primary radical center is about the same as that for abstraction of a hydrogen atom from the aldehyde by the neophyl radical. In similar cases, E_a for the latter process is 7–8 kcal./mole,[6] so that E_a (migration) can hardly exceed 8 kcal./mole.

An estimate of the heat of isomerization of the neophyl radical may be made by means of the following cycle.

	ΔH, kcal./mole
$H\cdot + C_6H_5C(CH_3)_2CH_2\cdot \longrightarrow C_6H_5C(CH_3)_2CH_3$	-95.5[7]
$C_6H_5CH_2CH(CH_3)_2 \longrightarrow C_6H_5CH_2\dot{C}(CH_3)_2 + H\cdot$	$+86.5$[8]
$C_6H_5C(CH_3)_2CH_3 \longrightarrow C_6H_5CH_2CH(CH_3)_2$	$+\ 0.3$[9]
$C_6H_5C(CH_3)_2CH_2\cdot \longrightarrow C_6H_5CH_2\dot{C}(CH_3)_2$	$-\ 8.7$

Further studies of this and related free radical processes, including gas phase experiments, are now in progress.

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(2) D. J. Cram, THIS JOURNAL, **71**, 3863 (1949).

(3) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and W. E. Vaughan, *Faraday Society Discussions*, No. 10, 242ff and 315 (1951).

(4) That exact proportionality to the initial aldehyde concentration was not observed may be due to an increased amount of rearranged dimer in the reaction in chlorobenzene.

(5) (a) M. S. Kharasch and H. C. Brown, THIS JOURNAL, **61**, 2142 (1939); (b) M. S. Kharasch and A. T. Read, *ibid.*, **61**, 3089 (1939).

(6) R. K. Brinton and D. H. Volman, *J. Chem. Phys.*, **20**, 1053 (1952).

(7) Assumed to be as in neopentane; E. I. Hormatz and E. R. VanArtsdalen, *J. Chem. Phys.*, **19**, 778 (1951).

(8) Assumed to be as in isobutane; J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

(9) E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 455 (1946).

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY FRANK H. SEUBOLD, JR.
EVANSTON, ILLINOIS

RECEIVED APRIL 30, 1953

ELECTROPHORETIC CONTRIBUTIONS TO THE DIFFUSION OF ELECTROLYTES

Sir:

The effect of electrophoresis on the diffusion coefficient of an electrolyte may be represented by the equation

$$D = (1 + c\partial \ln y_\pm/\partial c)\,(D^0 + \Delta_1 + \Delta_2 + \cdots + \Delta_n + \cdots)$$

where Δ_n represents the electrophoretic contribution involving the n^{th} power of the potential due to the "central" ion, and D^0 is the Nernst limiting value. In the theory due to Onsager and Fuoss[1] terms beyond Δ_2 are ignored, and the resulting formula is satisfactory for 1:1 electrolytes,[2] but fails to account for the experimental data for calcium chloride[3] and lanthanum chloride[4] even at higher dilutions. I have now obtained a general expression for Δ_n and have evaluated terms up to $n = 5$.

The expression may be abbreviated to

$$\Delta_n = (-1)^n \frac{F_n(\kappa a)}{|z_1 z_2|} \cdot \frac{(z_1^n t_2^0 + z_2^n t_1^0)^2}{\mathring{a}^n}$$

where $F_n(\kappa a)$ is a function only of κa and solvent properties, κa being the familiar dimensionless quantity of the Debye–Huckel theory; z_1 and z_2 are the algebraic valencies of cation and anion, respectively; t_1^0 and t_2^0 are the respective limiting transport numbers; and $\mathring{a}$ is the distance of closest approach of the ions, *expressed in Ångströms.* It turns out that $F_n(\kappa a)$ for aqueous solutions at 25° remains of a fixed order of magnitude (for a given κa) for all values of n up to at least $n = 5$. Hence the convergence of the series $\Sigma\Delta_n$ for small n is dependent upon the behavior of the function $(z_1^n t_2^0 + z_2^n t_1^0)^2/\mathring{a}^n$. It is easily seen that for 1:1 electrolytes with $\mathring{a}$ in the typical range of 3–5, convergence will be rapid. For higher valence

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(1) See H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943.

(2) H. S. Harned and R. L. Nuttall, THIS JOURNAL, **69**, 736 (1947).

(3) H. S. Harned and A. L. Levy, *ibid.*, **71**, 2781 (1949).

(4) H. S. Harned and C. A. Blake, *ibid.*, **73**, 4255 (1951).

types however there is no sign of convergence at $n = 2$, which explains the failure of the Onsager-Fuoss theory for calcium chloride and lanthanum chloride.

For potassium chloride the terms beyond Δ_2 are negligible; for calcium chloride at 0.005 molar the values are: $\Delta_1 = -0.019$, $\Delta_2 = +0.037$, $\Delta_3 = -0.016$, $\Delta_4 = +0.016$, $\Delta_5 = -0.010$, ... (the units being cm.^{2} sec.$^{-1}$ × 10^{-5}). For lanthanum chloride at 0.003 molar they are: $\Delta_1 = -0.033$, $\Delta_2 = +0.074$, $\Delta_3 = -0.071$, $\Delta_3 = +0.093$, $\Delta_5 = -0.096$, ...

A fuller account of this work will appear shortly.

CHEMISTRY DEPARTMENT
UNIVERSITY OF W.A. R. H. STOKES
NEDLANDS, WESTERN AUSTRALIA

RECEIVED APRIL 21, 1953

ANISOTROPY IN THE PARAMAGNETIC RESONANCE SPECTRUM OF PEROXYLAMINE DISULFONATE ION[1]

Sir:

In an earlier report[2] of the hyperfine splitting in the paramagnetic resonance absorption spectrum of $(C_6H_5)_3C^{13}$ attention was called to the fact that observations in liquid solutions fail to reveal important features of the phenomenon. We have since observed the paramagnetic resononce spectrum of the free radical ion peroxylamine disulfonate $(NO(SO_3)_2^=)$ in dilute solid solution in single crystals of diamagnetic potassium hydroxylamine disulfonate. In liquid solution the ion exhibits an absorption spectrum of three equally spaced equal intensity lines. The three lines result from the hyperfine interaction between the nitrogen nucleus (spin one) and the electron.[3] The interval between adjacent lines is 13 oersteds. In the single crystals (containing about 0.25 mole per cent. of the paramagnetic ion) the spectrum is highly anisotropic. The crystals, whose structure is under investigation by Professor Lindsay Helmholz and Mr. Merton Brooks, are monoclinic. When the external magnetic field is perpendicular to the two-fold axis of the crystal and makes an angle of about 45° with the "*c*" axis, three lines of equal intensity with interval 27 oersteds—more than twice the interval observed in liquid solutions—are seen. When the crystal is rotated by 90 degrees around the two-fold axis from the above orientation, the interval shrinks to six oersteds. At most other orientations the spectrum is complex, consisting of four or five lines. An explanation of the details of the dependence of spectrum on orientation of the crystal awaits completion of the crystal structure determination.[4] Nevertheless, sufficient information is available to permit the drawing of certain conclusions concerning the distribution of the unpaired electron in the molecule.

Interpretation of the experimental results depends on the fact that the hyperfine interaction consists of two parts, one isotropic, the other anisotropic. The former depends only on the non-vanishing component of the wave function at the nucleus, the latter only on the non-spherically symmetric components distant from the nucleus. If the electronic wave function of a free radical is expanded in atomic functions only s components contribute to the isotropic interaction, non s components to the anisotropic interaction. When the frequency of molecular tumbling is high compared with the frequency associated with the hyperfine interaction, only the isotropic part of the splitting is observed, the non-isotropic part averaging to zero.[5,6,7]

Thus the observed splitting in liquid solutions of $(C_6H_5)_3C^{13}$ demonstrates the existence of methyl carbon 2s component in the electronic function.[8] Experiments in single crystals are required for estimation of the non "s" components. In the peroxylamine disulfonate, both nitrogen 2s and 2p components are important. Their amplitudes will be estimated at another time.

WASHINGTON UNIVERSITY S. I. WEISSMAN
ST. LOUIS, MISSOURI DOROTHY BANFILL

RECEIVED APRIL 24, 1953

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[1] Assisted by the joint program of O.N.R. and A.E.C.

[2] S. I. Weissman and J. C. Sowden, THIS JOURNAL, **75**, 503 (1953).

[3] G. E. Pake, J. Townsend and S. I. Weissman, *Phys. Rev.*, **85**, 682 (1952); J. Townsend, S. I. Weissman and G. E. Pake, *ibid.*, **89**, 606 (1953).

[4] The magnetic observations suggest that two orientations of the peroxylamine disulfonate ion with respect to the crystal axis occur.

[5] See for instance, A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.*, **205**, 1935 (1951); N. Bloembergen, E. M. Purcell and R. V. Pound, *Phys. Rev.*, **71**, 466 (1947); H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

[6] In the cases here described the hyperfine frequency is in the neighborhood of 10^8 sec.$^{-1}$.

[7] The result is readily demonstrated for the case in which the external magnetic field is strong and spin orbit interaction is small. It is probably correct in the absence of these restrictions.

[8] The square of the amplitude of this component is probably between 0.05 and 0.10.