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

$$R_1\dot{C}O \xrightarrow{k_1} R_1\cdot + CO$$

$$R_1\cdot + R_1CHO \xrightarrow{k_2} R_1H + R_1\dot{C}O$$

$$R_1\cdot \xrightarrow{k_3} R_2\cdot$$

$$R_2\cdot + R_1CHO \xrightarrow{k_4} R_2H + R_1\dot{C}O$$

$$\frac{(R_2H)}{(R_1H)} \approx \frac{d(R_2H)}{d(R_1H)} = \frac{k_3}{k_2(R_1CHO)}\,.$$

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
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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: $\Delta_1 = -0.019$, $\Delta_2 = +0.037$, $\Delta_3 = -0.016$, $\Delta_4 = +0.016$, $\Delta_5 = -0.010, \ldots$ (the units being cm.^{2} sec.$^{-1} \times 10^{-5}$). For lanthanum chloride at 0.003 molar they are: $\Delta_1 = -0.033$, $\Delta_2 = +0.074$, $\Delta_3 = -0.071$, $\Delta_3 = +0.093$, $\Delta_5 = -0.096, \ldots$.

A fuller account of this work will appear shortly.

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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 resonance 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.

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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.