located at 6160 Å. in the Np(V) spectrum. Simple arguments based on crystal field effects do not appear adequate to interpret these observations.

The changes observed in the original spectrum of Np(V) when cations other than chromic are added to the solution are in themselves considered as evidence for complex ion formation. The results obtained with chromic ion provide additional evidence that such observations indicate the formation of a complex.

If we assume that the values of ϵ at 9800 Å. (presented in Table II) are a measure of the amount of Np(V) that does not interact, these data allow us to order the given set of cations as to the relative strength of their interaction with the Np(V) ion. Such an ordering is presented in Table II where it is evident that Al(III) has the weakest and Fe(III) the strongest interaction.

In addition to the observations presented in the experimental section no evidence was obtained for complex formation between Np(V) and either yttrium (3.0 *M*) or Ce(III), 2.0 *M*, in solutions of the perchlorate salts. This evidently precludes an attempt at a detailed correlation between relative bond strength and other properties characteristic of the trivalent cations such as crystal radii. However we can note that bond formation is observed when such radius is less than or equal to 0.81 Å. and not observed when such radius is greater than or equal to 0.93 Å.

It is apparent that the electronic configuration of the trivalent cation is of importance in the formation of these complexes. This is most clearly demonstrated if we recall that the crystal radii of Ga(III) and Fe(III) are almost equal and note the ordering in Table II. Additional discussion of this point would not be fruitful since, as Jorgensen[18] has pointed out, it is not readily apparent what importance is to be attached to molecular orbital contributions in bonding of complexes.

Studies of these complexes should provide information which may be of assistance in delineating properties of activated complexes for certain redox reactions. For example in the reduction of Np(V) by V(III)[19] and Np(III)[20] the relationship between crystal radii and complex formation is consistent with an inner sphere activated complex in the former and an outer sphere activated complex in the latter reaction.

It is of interest to note that Newton has obtained evidence for the existence of intermediates U(V)·Cr(III)[21] and Pu(V)·Fe(III)[22] during the course of kinetic studies. These intermediates are probably similar to the stable complexes previously discussed between Np(V) and the M(III) ions and suggests that the $(O\text{-}M\text{-}O)^+$ entity (and not detailed electronic configuration of the actinide atom) is the factor most important for the formation of such species.

In addition we may be able to use the Np(V) ion as a probe to increase our understanding of the properties in the first coördination sphere of selected cations. If the spectrum of the Np(V)·Cr(III) complex can be described by theory then comparison of the spectrum obtained with other trivalent cations might be used to obtain relative values for the effective electric field of these ions.

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Ionization and Dissociation Equilibria in Liquid Sulfur Dioxide. IX. *m*- and *p*-Neopentyl Derivatives of Triphenylchloromethane at 0.00°

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Analysis of conductance data by Shedlovsky's method provides values of $K_{\text{exp}} = (Ar_3C^+)(Cl^-)/[(Ar_3CCl) + (\overparen{Ar_3C^+Cl^-})]$ of 8.1 ± 0.5 × 10^{-4} and 3.7 ± 0.3 × 10^{-4} mole l.$^{-1}$ and of Λ_0 of 191.5 ± 1.3 and 182.4 ± 3.6 for mono-*p*-neopentyltriphenylchloromethane and di-*m*-neopentylphenylphenylchloromethane, respectively. From values of $K_1 = (\overparen{Ar_3C^+Cl^-})/(Ar_3CCl)$, calculated with the aid of Bjerrum's equation, $\Delta\Delta F_1$, measuring the effect of one alkyl group on the work of ionization of trityl chloride, is found to be -1.54 and -0.49 kcal. mole^{-1} for *p*- and *m*-neopentyl, respectively. Both values are essentially indistinguishable from the corresponding values for methyl. The data for these substituents and for *m*- and *p*-*t*-butyl can be rationalized in terms of joint action of inductive effect and hyperconjugation. They appear to be less consistent with Schubert's "steric inhibition of solvation" model.

Introduction

It has been established in prior papers of this series[2] that the influence of a substituent attached to the aromatic ring on the stability of the triarylcarbonium ion can be evaluated with considerable precision from conductance data. This paper is concerned with the *m*- and *p*-neopentyl groups. Because of our inability to obtain pure crystalline mono-*m*-neopentyltriphenylchloromethane, it was necessary to evaluate the effect of *m*-neopentyl

[1] Based in part on a portion of a dissertation submitted by Paul E. Rowe in fulfillment of a requirement for the Ph.D. degree, granted by Boston University in June 1959.

[2] *Cf.*, N. N. Lichtin and M. J. Vignale, *J. Am. Chem. Soc.*, **79**, 579 (1957), and earlier papers.

from the behavior of di-*m*-neopentylphenylphenylchloromethane.

Data.—The data of typical conductance experiments employing the internal dilution procedure[3] are presented in Table I. The values of K_{exp}, representing the equilibrium between free ions and the sum of covalent molecules and ion pairs (equations 1, where quantities in parentheses are activities), and of Λ_0, the limiting equivalent conductance, calculated from the data of three experiments for each of the two solutes by means of Shedlovsky's procedure,[4] are presented in Table II. Only data in the dilution range 2,000 to 50,000 l. mole^{-1} were employed in evaluating these constants. Shedlovsky's equation was solved by the method of least squares, taking $1/\Lambda S(Z)$ as the dependent variable.

TABLE I

CONDUCTANCE DATA OF TWO TYPICAL EXPERIMENTS

Mono-*p*-neopentyl trityl chloride		Di-*m*-neopentyl trityl chloride	
V, l. mole^{-1}	Λ,[a] mhos cm.^{2} mole^{-1}	V, l. mole^{-1}	Λ_0,[a] mhos cm.^{2} mole^{-1}
743	112.2	1143	92.5
1523	131.7	2334	115.1
3123	148.6	4761	134.1
6420	162.2	9707	149.2
13170	172.4	19790	160.8
27040	179.4	40340	169.4
55550	183.9	82210	177.6

[a] Corrected for conductivity of the solvent which fell in the range 3.5×10^{-8} to 15.2×10^{-8} mhos cm.$^{-1}$.

TABLE II

CONSTANTS CALCULATED BY SHEDLOVSKY'S PROCEDURE[4]

Compound	K_{exp},[a] mole l.$^{-1}$ $\times 10^4$	Λ^b_0, mhos cm.^{2} mole^{-1}
Mono-*p*-neopentyltrityl chloride	8.1 ± 0.5	191.5 ± 1.3
Di-*m*-neopentyltrityl chloride	3.7 ± 0.3	182.4 ± 3.6

[a] (Variances)$^{1/2}$ are for 95% confidence limits and were calculated from the variances in the slopes b and intercepts a of the linear Shedlovsky relationships via the equation, $S_K^2 = (a/b)^2\ [4\ S_a^2 + (a/b)^2\ S_b^2]$, where the S^2 terms represent variances; *cf.* O. L. Davies, "Statistical Methods in Research and Production," Oliver and Boyd, London, 1949, p. 37. [b] (Variances)$^{1/2}$ are for 95% confidence limits and were calculated from the variances in the intercepts of the linear Shedlovsky relationships.

$$\mathrm{Ar_3CCl} \underset{}{\overset{K_1}{\rightleftarrows}} \overparen{\mathrm{Ar_3Cl^+Cl^-}} \overset{K_2}{\rightleftarrows} \mathrm{Ar_3C^+ + Cl^-} \qquad (1)$$

$$K_{exp} = \frac{(\mathrm{Ar_3C^+})(\mathrm{Cl^-})}{(\mathrm{Ar_3CCl}) + (\overparen{\mathrm{Ar_3C^+Cl^-}})} = \frac{K_1K_2}{1 + K_1}$$

Discussion

Group effects, in the usual sense, influence only K_1. The magnitude of K_2, the dissociation constant of an ion pair, the binding force in which is presumably purely electrostatic, is essentially dependent on the geometries of the paired ions. Conductance data do not permit the separate evaluation of K_1 and K_2. It has been shown,[5-7] however, that, for solutions in liquid sulfur dioxide, the association behavior of a number of ionophores composed of spherical and tetrahedral ions adheres remarkably closely to Bjerrum's equation[8] when the Bjerrum distance of closest approach is identified with the appropriate sum of crystallographic or van der Waals radii. Ion pair dissociation constants involving carbonium ions have been calculated[2,9] with Bjerrum's equation, assigning Bjerrum distances of closest approach based on the assumption that a disk-shaped cation has an effective radius equal to its largest van der Waals radius about its center of gravity. Although this assumption has proved[6] to be less accurate than the identification of the Bjerrum and crystallographic radii of small spherical ions, dissociation constants involving large ions vary sufficiently gradually with interionic distance that the constants can be approximated with sufficient precision. Thus, for methylpyridinium picrate, substitution of the sum of the radii of the two disk-shaped ions defined as above (9.2 Å.) into Bjerrum's equation yields $K_{\mathrm{Bjerrum}} = 3.5 \times 10^{-3}$ mole l.$^{-1}$ at 0.175°. The corresponding value of K_{exp} based on conductance data is 2.9×10^{-3} mole l.$^{-1}$. It can be assumed that, although K_2 values calculated from Bjerrum's equation and ionic radii[10] may be in error by twenty five per cent. or more, the errors are of the same sign and similar magnitude for a series of substituted triphenyl carbonium chlorides. Because the K_2 values are similar and much larger than K_{exp} these errors have little influence on the relative magnitudes of K_1 values calculated with their aid. Table III presents assumed cationic radii (chloride radius is taken as 1.8 Å.) and values of K_1 and K_2 for the neopentyl substituted triphenylchloromethanes as well as the unsubstituted compound and methyl[11] and *t*-butyl[9] derivatives. K_1 values and free energies of ionization for *mono*-substituted trityl chlorides relative to those for the parent compound, $(K_X/K_H)_1$ and $\Delta\Delta F_1$, respectively, are presented, including as a substituent *m*-neopentyl. In the latter case, it has been assumed that two substituents alter the free energy of ionization by twice the amount that one would, an assumption which appears to be supported by our earlier

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[3] N. N. Lichtin and P. D. Bartlett, *J. Am. Chem. Soc.*, **73**, 5530 (1951).

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

[5] N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, **60**, 160 (1956).

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[7] N. N. Lichtin and K. N. Rao, *J. Phys. Chem.*, **64**, 945 (1960).

[8] N. Bjerrum, *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.* **7**, No. 9, 1 (1926). *Cf.*, H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1958, p. 70.

[9] N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, **60**, 164 (1956).

[10] X-Ray diffraction studies of triphenylcarbonium perchlorate have established that the three phenyl groups lie in planes rotated 32° in the same direction out of the plane defined by the central carbon atom and the three phenyl carbon atoms attached to it (private communication from K. Eriks. For a preliminary report see Abstracts of papers, Summer Meeting of the American Crystallographic Association, Cornell University, Ithaca, N. Y., July, 1959, p. 17).

[11] N. N. Lichtin, E. S. Lewis, E. Price and R. R. Johnson, *J. Am. Chem. Soc.*, **81**, 4520 (1959).

investigations involving *p*-*t*-butyl,[9] *p*-phenyl[9] and *p*-chloro[2] as well as the behavior of related systems,[12] and the constants for the unavailable mono-*m*-neopentyl compound have been calculated from the data for the disubstituted compound.

TABLE III

DISSOCIATION AND IONIZATION CONSTANTS OF *m*- AND *p*-ALKYL DERIVATIVES OF TRIPHENYLCHLOROMETHANE AT 0°

Substituents	r^+, Å.	K_2, mole l.$^{-1}$ × 10^3	K_1 × 10^2	$(K_X/K_H)_1$ for one substituent	$-\Delta\Delta F_1$ kcal. mole^{-1}
None[a]	6.5	2.88	1.46	(1.00)	(0.00)
Mono-*m*-methyl[a]	6.6	2.92	3.37	2.31	.45
Mono-*m*-*t*-butyl[b]	8.1	3.78	4.79	3.28	.65
Di-*m*-neopentyl	9.2	4.50	8.86	2.46[d]	.49[e]
Mono-*p*-methyl[c]	7.4	3.36	23.4	16.0	1.51
Mono-*p*-*t*-butyl[b]	8.3	3.90	22.5	15.4	1.49
Mono-*p*-neopentyl	8.6	4.09	24.7	16.9	1.54

[a] Taken from ref. 2. [b] Taken from ref. 9. [c] K_{exp} taken from ref. 11 and r^+ from ref. 2. [d] $(8.86/1.46)^{1/2}$; *cf.*, text for explanation. [e] For one *m*-neopentyl group.

In recent years, interpretation of the effects of alkyl groups bound to the benzene ring on chemical reactions in the ring or in side chains and on physical properties has received a great deal of attention. That this large effort has not yet produced wide areas of agreement is well illustrated by the divergent views presented at the Bloomington Conference on hyperconjugation.[13] Quite obviously, the few new data presented here cannot provide the basis for any definitive conclusion. It is, however, of interest to consider the relationship of the data to some current concepts.

The effects of *m* and *p*-methyl and *t*-butyl groups on the ionization of trityl chloride were originally rationalized[3] in terms of the inductive effect, the principal effect acting from the *m*-position, and hyperconjugation, assumed to be responsible for the major part of the influence of *p*-substituents. Bartlett[14] subsequently elaborated this analysis somewhat and quantitatively estimated the relative effectiveness of C–H and C–C hyperconjugation in this system. More recently, Mulliken[15] has emphasized that the quantum mechanical theory of hyperconjugation includes π-delocalization from both C–H and C–C bonds. The present results are consistent with this approach and indicate that neopentyl has an inductive effect similar to that of methyl and significantly smaller than that of *t*-butyl, while its hyperconjugation effect is indistinguishable from that of methyl but greater than that of *t*-butyl. This conclusion can be stated quantitatively in terms of a treatment by Taft and Lewis[16] which is based on the same viewpoint. Thus, with the aid of equations 2 and 3, where α is taken as 0.1, it is found that R, the resonance constant, is 0.93, 0.75 and 0.93 for methyl, *t*-butyl and neopentyl, respectively, while I, the inductive

$$R = \frac{1}{1 - \alpha} \log k^{\mathrm{p}}/k^{\mathrm{m}} \qquad (2)$$

$$I = \frac{1}{1 - \alpha} [\log k^{\mathrm{m}}/k_0 - \alpha \log k^{\mathrm{p}}/k_0] \qquad (3)$$

constant, is 0.27, 0.44 and 0.30 for the substituents in the same order. One is tempted to speculate about the reason for identical values of R for neopentyl and methyl but such speculation is very likely not justified by the precision of the K_{exp} values and the several assumptions involved in calculating K_1 and R.

The sensitivity of the relative magnitudes of alkyl effects to the nature of the chemical or physical process under investigation, and even to changes in solvent or temperature is well established.[17] Comparison with the data of Shiner and Verbanic[17a] concerning solvolysis of alkylbenzhydryl chlorides establishes that the neopentyl group is no exception to this phenomenon. Analysis of alkyl group influences in terms of inductive effects and C–H and C–C hyperconjugation must be performed with the assumption that the relative proportions and intensities of these interactions depend in a complicated way on the total system.

Other concepts have been offered as alternatives to hyperconjugation.[17b,18] Among these, the views of Schubert can be applied to the present data. Schubert assumes that bulky alkyl groups interfere with solvation and that this effect is superimposed upon their intrinsic electron releasing capacity which is regarded as increasing in the "inductive order." Solvent-solute interactions are presumed to be most intense at the *o*- and *p*-positions of the carbonium ion (or carbonium ion-like activated complex) so that bulky groups at these positions should be most effective in countering electron release. The data of Table III for *t*-butyl and methyl substituted trityl chlorides are consistent with this analysis, if one assumes that the fact that *p*-alkyl groups have larger effects than *m*-alkyl groups is a consequence of more intense local polarization of the former. The fact that neopentyl and methyl have very nearly the same effect in both the *m*- and *p*-positions is not readily explained in these terms. It is conceivable that *t*-butyl interferes with solvation more extensively than does neopentyl—as must be assumed to account for the results—but it is not plausible that methyl and neopentyl interfere equally. In the absence of precise information on the entropies and enthalpies of ionization, however, a thorough comparison of the effects of alkyl groups on the ionization of trityl chloride with Schubert's ideas cannot be made.

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Experimental

Conductance Measurements.—Procedures, solvent and equipment were essentially the same as those which have been described[2,5,19] previously. The conductance cell, improved by exclusion of mercury wells and in other minor ways, is described elsewhere.[20] The temperature of the oil thermostat was controlled at 0.00 ± 0.02.

Mono-*p*-neopentyltriphenylchloromethane.—*p*-Bromopivalophenone was prepared by the method of Pearson[21] in 54% yield from pivalonitrile and the mono-Grignard reagent derived from *p*-dibromobenzene, b.p. 108–111° at 3 mm. $n^{24}\mathrm{D}$ 1.5440, m.p.[22] of hydrazone, recrystallized twice from ethanol, 139.2–141.0°. Reduction by the Huang-Minlon[23] modification of the Wolff-Kishner reaction yielded *p*-bromoneopentylbenzene, typically in 57% yield, b.p. 96–98° at 3 mm. $n^{25}\mathrm{D}$ 1.5240. *Anal.* Calcd. for $C_{11}H_{15}Br$: C, 58.1; H, 6.7; Br, 35.2. Found[24]: C, 58.1; H, 6.7; Br, 35.2. Debromination by acid hydrolysis of the Grignard reagent yielded neopentylbenzene, b.p. 184° at 1 atm., $n^{25}\mathrm{D}$ 1.4850, m.p. of the mono-acetylamino derivative, prepared as described below, 162.5–164°. Neopentylbenzene prepared by the method of Bygden[25,26] by Grignard coupling of benzyl and *t*-butyl chlorides boiled at 182–184°, had $n^{25}\mathrm{D}$ 1.4855 and gave a mono-acetylamino derivative melting at 163–164°, undepressed by admixture of the acetylaminoneopentylbenzene derived from *p*-bromoneopentylbenzene. Attempts to convert the latter compound to *p*-bromobenzoic acid by refluxing for 100 hr. with aq. alkaline $KMnO_4$ or for 140 hr. with aq. acid $Na_2Cr_2O_7$ were unsuccessful.

Mono-*p*-neopentyltriphenyl carbinol was prepared by reacting *p*-neopentylphenyl Grignard reagent (prepared from Dow "super pure" sublimed magnesium) with benzophenone in anhydrous ether under an atmosphere of dry nitrogen. After a 2 hr. reflux period, the mixture was worked up in the conventional way. The residue remaining after removal of volatiles by steam distillation was subjected to a lengthy fractional crystallization process[27] which provided a 15% yield of white crystalline product, m.p. 99–100°. *Anal.* Calcd. for $C_{24}H_{26}O$: C, 87.2; H, 7.9. Found[24]: C, 87.0; H, 7.9.

Conversion of the carbinol into the chloride was effected by refluxing 1.30 g. (0.0039 mole) with 2.5 ml. (0.035 mole) of freshly distilled acetyl chloride in 5 ml. of 1:1 ether–petroleum ether for 2 hr. and refrigerating over night. Recrystallization from 30 ml. of 4:1 ether–petroleum ether and drying in an Abderhalden apparatus at 56° and 10^{-3} mm. provided 0.52 g. (0.0015 mole, 38%) of chloride, m.p. 129.5–130°. *Anal.* Calcd. for $C_{24}H_{25}Cl$: hydrolyzable Cl, 10.16. Found[11]: Cl, 10.08.

Other *p*-neopentylphenyl derivatives isolated and characterized in this work are described elsewhere.[27] These include mono-*p*-neopentyltriphenylmethyl ether, 4,4′-dineopentylbiphenyl, di-*p*-neopentyltriphenyl carbinol[28] and tri-*p*-neopentyltriphenyl carbinol.[29]

Di-*m*-neopentylphenylphenylchloromethane.—The preparation of this compound and of other *m*-neopentyl compounds was based on *m*-bromoneopentyl-benzene which was obtained by deaminating the appropriate bromoneopentylanilines which were, in turn, synthesized in a fashion analogous to the preparation of 3-bromo-4-aminotoluene.[30] Three hundred twenty five gram portions of neopentylbenzene (2.2 moles), prepared by Bygden's method,[25] were nitrated by adding a mixture of 222 cc. of concd. nitric acid and 265 cc. of concd. sulfuric acid dropwise with mechanical stirring at such a rate that the mixture remained at 50–60°. Stirring was continued at 70° for ten minutes after complete addition and then at room temp. overnight and the product was worked up in the usual manner. It is not necessary to separate isomeric neopentylnitrobenzenes in order to prepare *m*-bromoneopentylbenzene and, in most experiments, no separation was effected. For purposes of characterizing previously unreported intermediates, the isomers were separated in one experiment and carried through subsequent steps independently, as described below. The same reactions were carried out similarly with the mixed isomers. Rectification of the nitration product on a three foot glass helix-packed column at 3 mm. yielded 105 g. (0.55 mole) boiling at 106–111°, $n^{24}\mathrm{D}$ 1.5157, assumed to be *o*-neopentylnitrobenzene, 14 g. (0.07 mole) boiling at 111–118° and 253 g. (1.31 mole) boiling at 118–124°, $n^{24}\mathrm{D}$ 1.5223, assumed to be *p*-neopentylnitrobenzene,[31] a total of 1.93 mole or 88%. Approximately 50 g. batches of neopentylnitrobenzene in 100 cc. of 95% ethanol were hydrogenated at 3 atm. in the presence of 1 g. of freshly prepared Raney nickel. Products were isolated in approximately 85% yield after vacuum rectification. The product presumed to be *o*-neopentylaniline boiled at 91–93° at 3 mm., $n^{21}\mathrm{D}$ 1.5391. The presumed *para* compound solidified at room temperature. A solution in CS_2 of presumed *o*-neopentylaniline absorbed strongly at 735–770 cm.$^{-1}$ with λ_{max} at 750 cm.$^{-1}$. A solution of presumed *p*-neopentylaniline absorbed strongly at 810–850 cm.$^{-1}$, with λ_{max} at 850 cm.$^{-1}$ and weakly at 755–760 cm.$^{-1}$. These spectra are consistent[32] with the assigned structures. Acetylation of this product on a half mole scale with acetic anhydride and sodium acetate in aqueous hydrochloric acid, followed by crystallization from 95 percent ethanol, provided a 75% yield of presumed *p*-neopentylacetanilide, white flakes, m.p. 165–165.5°.[26] *Anal.* Calcd. for $C_{13}H_{19}NO$: C, 76.1; H, 9.3; N, 6.8. Found[33]: C, 76.0; H, 9.3; N, 6.8. A wasteful fractional crystallization from aqueous ethanol of the product of acetylation of presumed *o*-neopentylaniline provided a 38% yield of presumed *o*-neopentylacetanilide, white needles, m.p. 121–123°. *Anal.* Found[33]: C, 76.0; H, 9.2; N, 6.9. Treatment of the neopentylacetanilides in glacial acetic acid at room temp. with somewhat less than one mole of bromine in the presence of iron powder afforded yields of bromo derivatives in the vicinity of 90%. Presumed 2-bromo-4-neopentylacetanilide, recrystallized from benzene, white flakes, melted at 122–124°. Deacetylation was effected by transesterification with ethanolic HCl and, from 2-bromo-4-neopentylacetanilide, yielded white needles melting at 54–55°, presumably 2-bromo-4-neopentylaniline. Deamination of the individual or mixed bromoneopentylanilines was effected by reduction of the diazonium ions with hypophosphorous acid. A solution of 73 g. (0.30 mole) of bromoneopentylanilines in 700 cc. of glacial acetic acid containing 40 cc. of concd. sulfuric acid was added at 0–5° to a solution of 10 g. (0.145 mole) of $NaNO_2$ in 100 cc. of water and 400 cc. (3.8 moles) of 50% hypophosphorous acid. After one hour at 0°, a solution of 30 g. (0.435 mole) of $NaNO_2$ in 100 cc. of water was added slowly. The reaction mixture was then left at room temperature overnight before being worked up. Vacuum distillation yielded 39.5 g. (57%) of crude *m*-bromoneopentylbenzene, b.p. 78–82° at 2 mm. The product was purified by passage, in ligroin solution, through an alumina column followed by vacuum rectification. The fraction boiling at 80–81° at 2 mm., $n^{22}\mathrm{D}$ 1.5232, was employed in preparation of carbinols. A solid byproduct isolated from the first distillation is assumed to be 3,5-dibromoneopentyl benzene, b.p. 123–125 at 3 mm., m.p. 43–44.5°.

Di-*m*-neopentylphenylphenyl carbinol was prepared by reacting *m*-neopentylphenyl Grignard reagent (prepared from Dow "super pure" sublimed magnesium) with ethyl benzoate in anhydrous ether under a nitrogen atmosphere. The mixture was refluxed for two hours after addition of the

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(27) *Cf.*, P. E. Rowe, "Synthesis of Neopentyl Derivatives of Triphenyl Carbinol and the Kinetics of Bamberger's Reaction," doctoral dissertation, Boston University, 1959, pp. 48–50, for details.

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(32) C. W. Young, R. B. Duval and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

(33) Analysis by K. Ritter, Basel, Switzerland.

ester was complete. All attempts to obtain pure crystals from the yellow glass remaining after working up the mixture and steam distilling failed. Nine tenths of a gram (0.0023 mole) of the glass was refluxed for 90 min. with 8 cc. of acetyl chloride in 20 cc. of anhydrous thiophene-free benzene. The product was treated with decolorizing carbon, filtered, evaporated almost to dryness, crystallized from anhydrous petroleum ether and dried under vacuum at 54°, yielding white crystals melting at 93.5–95°. *Anal.* Calcd. for $C_{29}H_{3}Cl$: C, 83.1; H, 8.4; Cl, 8.47. Found[24]: C, 82.7; H, 8.6; Cl, 9.2. This product was passed through charcoal in anhydrous petroleum ether, recrystallized from this solvent and dried at 10^{-3} mm. and 56° to give white crystals melting at 95.5–96.0° (uncorr.). *Anal.* Found[11]: hydrolyzable chloride, 8.65.

Crystalline mono-*m*-neopentyltriphenyl carbinol, m.p. 53–56°, was obtained with great difficulty[34] but attempts to convert it to crystalline chloride were not successful.

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[34] Cf., ref. 27, pp. 57–60.

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Potential Method for the Determination of Electron Affinities of Molecules: Application to Some Aromatic Hydrocarbons

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One of the principal aims of this investigation is to establish the fundamental nature of the electron capture by molecules occurring in a detector used in gas chromatography. The interpretation is developed in terms of an equilibrium between the neutral molecules and the electrons. The relationship between the electron capture coefficients and the electron affinities of molecules is presented. The results for a series of aromatic hydrocarbons are compared to the half wave reduction potentials. If certain assumptions are made concerning the ratio of the partition functions of the gaseous negative ion of the molecule to the neutral gaseous molecule, the electron affinity of the molecule can be estimated. This has been carried out for anthracene and other aromatic hydrocarbons, and the results compare favorably with recent theoretically calculated values.

Within the past year and a half, an electron capture cell has been developed by Lovelock primarily for use as a sensitive detector in gas chromatography.[1] The detection of a compound is based upon its ability to capture thermal electrons. The relative magnitude of capture of an electron has been expressed in terms of the electron absorption or capture coefficient. The electron absorption coefficients of numerous compounds have been measured by this technique.[2,3] Up to this time, the functional relationship of this parameter with other fundamental physical properties of molecules has not been elucidated. The purpose of this paper is to discuss a relationship between the electron absorption coefficient and the electron affinity of a molecule. The electron affinity is defined here in the usual rigorous way as the energy associated with the process when a gaseous molecule captures an electron to produce a gaseous ion. Previous references to electron capture detectors employing the terminology electron affinity[1-3] have been made relative to the functional nature of the process and not relative to the energy involved in the process.

In general, it has been assumed that a molecule can capture an electron by either of two processes: (1) a nondissociative process whereby a gaseous negative ion of the molecule is formed, or (2) a dissociative process in which a portion of the molecule forms an independent gaseous ion and the remainder of the molecule exists at least temporarily as a radical in the gaseous state. The discussion in this paper will be restricted to the former process.

Heretofore, there has been no accurate and definitive method for the measurement of the electron affinity of complex molecules. The best estimate of this parameter has been accomplished by measurement of the polarographic half wave reduction potential. For example see Matsen[4] and references therein. However, as Matsen has pointed out,[5] in order to obtain the true electron affinity of the molecule from the half wave reduction potential, it is necessary to evaluate the difference in energy of solution of the neutral molecule and the negatively charged molecular ion. Unfortunately, it is difficult to evaluate this difference in energy of solution. For this reason, it is advantageous to work in the gaseous phase where this complication does not exist.

For the experimental details of the technique for measuring electron absorption coefficients, the original references should be consulted.[1,2] Our interpretation of the capturing process of an electron by a molecule is based on the establishment of an equilibrium between the neutral gaseous molecules, the free thermal electrons, and the gaseous negative ions of the molecule

$$AB + e^- = AB^- \qquad (1)$$

where AB represents the neutral molecule. The corresponding ideal gas equilibrium expression would be

$$K = [AB^-]/[AB][e^-] \qquad (2)$$

If the electron absorption coefficient is relatively small, the initial concentration of neutral molecules *a* will not be significantly diminished through

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[1] J. E. Lovelock, *Nature*, **189**, 729 (1961).

[2] J. E. Lovelock and N. L. Gregory, "Proceedings International Gas Chromatography Symposium," Lansing, Michigan, June 1961, Academic Press, Inc., New York, N. Y., p. 151.

[3] J. E. Lovelock, A. Zlatskis and R. S. Becker, *Nature*, **193**, 540 (1962).

[4] F. A. Matsen, in "Proceedings of 1957 Conference on Carbon," Pergamon Press, New York, N. Y., 1957, pp. 21–26.

[5] F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1955).