tion occur, although the efficiency of the two processes is reduced under these conditions.

In the very large number of compounds that have been examined by the present technique, aromatics are generally quite reactive whereas aliphatics such as cyclohexane exchange very slowly. A representative number of compounds is included in Table I to illustrate the type of reactivity to be expected, the data being reported in such a manner as to indicate relative rates of reaction; thus relatively low exchange temperatures are shown together with low deuteration. If the temperature is raised to 100–110° and the time of exchange increased slightly, equilibrium isotope incorporation is readily achieved in the active aromatic hydrogen positions of all compounds listed. A comparison of the rates of exchange of toluene and chlorobenzene (Table I) shows conclusively that the reaction is not acid catalyzed. The degree of exchange is not markedly influenced by the electronic character of the substituent (toluene *vs.* trifluorotoluene). This conclusion is further supported by the isotope orientation in chlorobenzene, *t*-butylbenzene, and trifluorotoluene where the exchange is exclusively *meta* and *para*, as indicated by both the cutoff in the low-voltage mass spectrum and nmr data. For many of the monosubstituted benzenes, there is a remarkable similarity in isotope orientation between the present homogeneous platinum(II) system and heterogeneous platinum-catalyzed exchange.[4] For certain other compounds there are significant differences in exchange properties from the two procedures; thus as a potential isotopic hydrogen labeling tool it is predicted that the homogeneous technique will replace heterogeneous methods for many compounds and also act as a complementary procedure for the labeling of many others. A detailed summary of the advantages of the present procedure together with a discussion of the mechanistic implication of the work with respect to fundamental catalysis will be published in a series of papers elsewhere.

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Contact and Solvent-Separated Ion Pairs of Carbanions. IV. Specific Solvation of Alkali Ions by Polyglycol Dimethyl Ethers

Sir:

We recently reported that variations in temperature and solvent composition caused reversible changes in the ultraviolet and visible absorption spectra of solutions of carbanions and radical anions.[1] The changes, showing distinctly separate absorption maxima (particularly pronounced with fluorenyl salts), were attributed to the existence of a rapid equilibrium between contact or intimate ion pairs (C^-,M^+) and solvent-separated ion pairs ($C^-||M^+$). The ratio of the fractions of the two kinds of ion pairs was found to be a sensitive function of the basicity and geometrical structure of the solvating molecules.

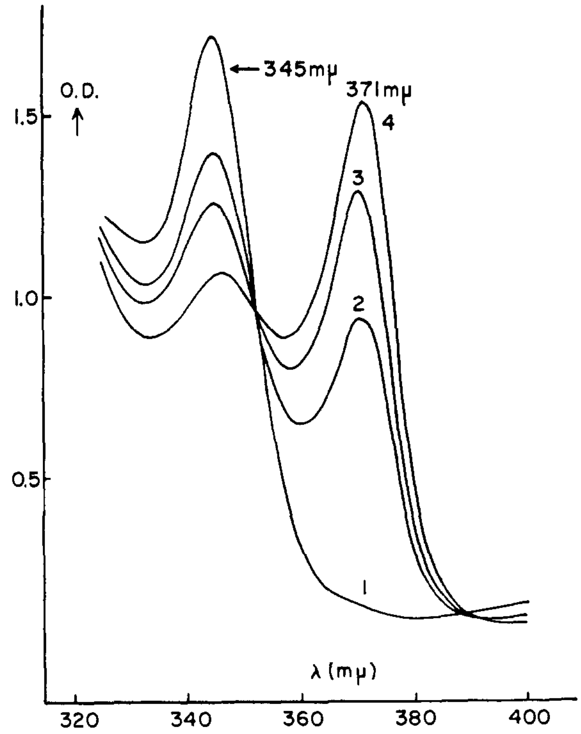

Figure 1. Spectrum of F^-,Li^+ in mixtures of dioxane and $CH_3O(CH_2CH_2O)_3CH_3$; $[F^-,Li^+] \approx 1.4 \times 10^{-3}$ *M*. Curve 1: pure dioxane; curves 2, 3, and 4 represent solutions with [PGDE] = 6.46 × 10^{-3} *M*, 11.3 × 10^{-3} *M*, and 24.3 × 10^{-3} *M*, respectively.

We have now investigated a series of polyglycol dimethyl ethers (PGDE) of the formula $CH_3O(CH_2CH_2O)_xCH_3$ with respect to their behavior in solvating alkali cations. These molecules are expected to be powerful solvating agents because of the presence of multiple coordination sites within the same molecule.[2,3] In our experiments, a solution of fluorenyllithium in dioxane (only contact ion pairs are observed in this solvent) was titrated under vacuum with a solution of the same salt in a mixture of dioxane and the respective polyglycol ether. The latter mixture was prepared so as to contain close to 100% solvent separated ion pairs. After each addition the optical spectrum was recorded. (With fluorenylsodium, some difficulties were encountered with dioxane as solvent, and THF was therefore used.)

An example involving triethylene glycol dimethyl ether is shown in Figure 1. The appearance of an isosbestic point confirms the stoichiometry of the reaction. The ratio of the fraction of the solvent-separated ion pair (371 mμ) over that of the contact ion pair (345 mμ) can be determined since the "pure" ion-pair spectra are known. Let us denote by *n* the number of PGDE mole-

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(2) J. Ugelstad and O. A. Rokstad, *Acta Chem. Scand.*, **18**, 474 (1964).

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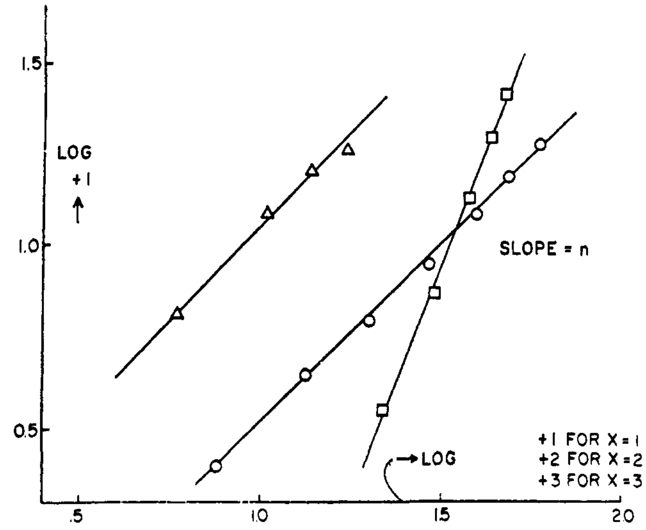

Figure 2. Plots of log [$C^-\|M^+$]/[C^-,M^+] (ordinate) *vs.* log [PGDE] (abscissa) for F^-,Li^+ in mixtures of dioxane and $CH_3O(CH_2CH_2O)_x$-CH_3.

cules participating in the equilibrium

$$C^-,M^+ + n\text{PGDE} \rightleftarrows C^- \| M^+ \qquad (K_i)$$

A plot of log [$C^-\|M^+$]/[C^-,M^+] *vs.* log [PGDE] should then yield a straight line with slope n. A few examples of such plots are shown in Figure 2, while the values for n and K_i for both fluorenyllithium and sodium are reported in Table I.

Table I. Solvent-Separated Ion-Pair Formation of Fluorenyllithium and Fluorenylsodium with Polyglycol Dimethyl Ethers (PGDE)[a]

PGDE	Fluorenyllithium[b] K_i[c]	n	Fluorenylsodium[b] K_i[c]	n
$CH_3O(CH_2CH_2O)CH_3$	0.055	2.4		
$CH_3O(CH_2CH_2O)_2CH_3$	3.1	0.98	1.3	0.77 (?)
$CH_3O(CH_2CH_2O)_3CH_3$	130	1.03	6.8	0.85
$CH_3O(CH_2CH_2O)_4CH_3$	185	0.96	125	0.96
Dimethyl sulfoxide[1]	230	1.04		

[a] [F^-,M^+] ≈ 1.5×10^{-3} M; $T = 25°$. [b] For F^-,Li^+, dioxane was used as a solvent, for F^-,Na^+, THF was used. [c] K_i = [$F^-\|M^+$]/{[F^-,M^+][PGDE]^n}.

It appears that for $x \geqslant 2$, *i.e.*, when three or more coordination sites are available, the value for n is essentially 1, indicating that only one polyglycol ether molecule appears to be coordinated with the Li^+ or Na^+ ion in the solvent-separated ion pair. It is interesting to note that for the fluorenyllithium salt a large increase in the solvating power of the polyglycol ether is observed when four coordination sites are available for solvation. An increase in the number of coordination sites to five ($x = 4$) only increases the K_i value slightly. This indicates that Li^+ is probably coordinated with not more than four oxygen atoms (not necessarily in a tetrahedral arrangement). The triethylene glycol dimethyl ether molecule acts as a solvent cage for Li^+ and all four oxygen atoms are apparently utilized in the solvation. For the sodium ion the strongest increase in the solvating power occurs when the number of oxygen atoms increases from 4 to 5. The interaction between oxygen and Na^+ is considerably weaker than with Li^+, and a coordination with five or possibly six oxygen atoms may be required to favor solvent-separated ion-pair formation.

Calculations indicate that, contrary to previous observations involving dimethyl sulfoxide,[1] the contact ion pair F^-,Li^+ appears not to be peripherally solvated by a PGDE molecule as long as $x \geqslant 3$. For $x < 3$ a larger excess of PGDE is required, and the possibility of solvated contact ion pairs cannot be excluded.

The high solvating power of the polyglycol ethers (some are solvating alkali ions as good as dimethyl sulfoxide) is essentially due to a favorable entropy of solvation. Temperature-dependence studies of the equilibrium constant K_i for F^-,Na^+ show that the ΔH_i of solvation in a THF–tetraethylene glycol dimethyl ether mixture amounts to -7 kcal/mole (similar to that in pure THF[1]), while ΔS_i of solvation amounts to -12 eu compared to -40 eu in pure THF.

The specific solvation of alkali ions by the polyglycol ether molecules can also be studied by nmr. For example, fluorenyllithium in THF exists at room temperature for about 80% as a solvent-separated ion pair, and in a 0.3 M solution about 10% of the THF molecules are coordinated with the Li^+ ion, assuming four molecules/Li^+ ion. In such a solution the THF peaks are shifted upfield by about 8–10 cps compared to those of pure THF, a behavior also observed for THF solutions of alkali tetraphenylboron salts.[4] When an equimolar quantity of polyglycol ether (x = 3 or 4) is added to this solution, the THF peaks shift downfield again, close to their position in pure THF, while the peaks of the PGDE are strongly shifted upfield by as much as 30 cps (see Table II).

Table II. Nmr Chemical Shifts[a] in Mixtures of THF and Polyglycol Dimethyl Ethers (PGDE) in the Presence of 0.3 M Fluorenyllithium[b]

System	THF peaks α-CH_2	β-CH_2	PGDE peaks CH_3	ext CH_2	int CH_2
THF[c]	3.62	1.73			
PGDE (x = 3)			3.27	3.49	3.53
PGDE (x = 3)			3.27	3.49	3.53
F^-,Li^+-THF	3.43	1.61			
F^-,Li^+-THF-PGDE (x = 3)[d]	3.58	1.74	2.96	2.99	3.00
F^-,Li^+-THF-PGDE (x = 4)[d]	3.58	1.70	2.77	2.87	2.95

[a] Chemical shifts in parts per million downfield from TMS. [b] Temperature, 40°. [c] THF contains 0.3 M fluorene. [d] The assignments of the shifted PGDE peaks is not certain. A reversal of the relative positions of the peaks may have occurred (see ref 5) but this could not be established with certainty. Some of the peaks move considerably farther upfield at lower temperatures.

Apparently the THF molecules around Li^+ are now replaced by the PGDE molecule. At equimolar concentrations, particularly on lowering the temperature, essentially all PGDE molecules (at least for $x \geqslant 3$) are coordinated with Li^+. Hence, even if the optical spectra of both solutions are the same (solvent-separated ion pairs are involved in both THF and its mixture with PGDE), the nmr can decide which of the two molecules in the mixture preferentially solvates the cation.

The coordination with Li^+ itself would be expected to lead to a downfield shift due to an increased electronegativity on the oxygen atoms (as observed with compounds like $NaClO_4$, $LiClO_4$, etc.[4]). However, in

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the solvent-separated fluorenyl ion pair the coordinating ether molecules are very close to the aromatic ring, and the shielding effect due to the aromatic ring current apparently causes the strong upfield shift. These shifts are reminiscent of those found for dimethoxyethane in mixtures of benzene with fluorenyllithium,[5] although it is probable that in this case solvated contact ion pairs are involved.

Acknowledgment. Support of this work by the Research Foundation of the State University of New York and by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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Activation Volumes of Homolytic Scission Reactions. *t*-Butyl Phenylperacetate

Sir:

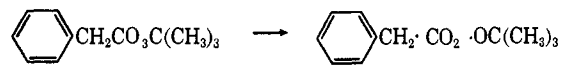
Homolytic scission reactions are characterized by relatively large positive activation volumes.[1-6] With the exception of the *t*-butyl peroxide data in benzene and carbon tetrachloride,[1,6] these have been presumed to reflect the volume difference between ground and transition state for homolytic scission. However, recent work now suggests that none of these data (with the possible exception of that for AIBN) directly measures the pressure dependence of the bond-scission process.

The effective assumption made in identifying ΔV^* with this process (k_1) is that internal return (k_{-1}) does not occur. However, this has now been demonstrated

$$\text{A-B} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (\text{A}\cdot\ \text{B}\cdot) \xrightarrow{k_2} \text{A}\cdot + \text{B}\cdot \qquad (1)$$

to be significant in atmospheric pressure solution phase decomposition of acetyl peroxide,[7,8] *p*-nitrophenylazotriphenylmethane (NAT),[8] and *t*-butyl peroxide,[9] suggesting that this feature characterizes the majority of the systems studied as a function of pressure.[1,10] Observed decomposition rate constants are therefore not equal to k_1 but rather to $k_1/(1 + k_{-1}/k_2)$, and the activation volumes represent a composite pressure effect. Increasing pressure most certainly decreases k_1, and other studies of geminate recombination reactions[2,11,12] show that the ratio k_{-1}/k_2 is increased. Thus, the values[1] of ΔV^* may be significantly larger than the values of ΔV_1^*.[13]

In principle, any system undergoing a homolytic scission of only a *single* chemical bond is subject to internal return. However, volumes of activation for concerted two-bond homolyses in which a stable molecule is produced should reflect the volume changes associated with bond breaking since internal return to starting material will be unlikely. Available data indicate that *t*-butyl phenylperacetate decomposition follows this latter mechanistic path.[14-17]


(2)

Kinetic studies of the thermal decomposition (79.55°) of *t*-butyl phenylperacetate (0.10 *M*) in cumene and chlorobenzene have yielded the data in Table I and Figure 1. The resulting activation volumes are +1.0 ± 0.1 cc/mole (cumene) and +1.5 ± 0.3 cc/mole (chlorobenzene).[18] We suggest that these very low values reflect the absence of internal return and are a good approximation of ΔV_1^*.[17] In support of this hypothesis, preliminary data at 1 and 4000 atm for the thermal decomposition (79.55°) of *t*-butyl perbenzoate (a one-bond scission process)[14] yield activation volumes of +11 ± 2 cc/mole (cumene) and +13 ± 4 cc/mole (chlorobenzene).

Table I. *t*-Butyl Phenylperacetate Kinetic Data at 79.55°

	$k \times 10^4$, sec^{-1}	
P, atm	Cumene[a]	Chlorobenzene[a]
1	0.66	1.07
2000	0.62	0.95
4000	0.56	0.91

[a] Reactions followed by infrared;[16] 1-atm data collected under the same conditions as the high-pressure data.

Possible competing induced decomposition and cyclic rearrangements (*e.g.*, the Criegee rearrangement) for *t*-butyl phenylperacetate would be pressure accelerated. However, the activation volumes are virtually identical in cumene and chlorobenzene, although induced decomposition would be more likely in chlorobenzene. Product data at 1 and 4000 atm in both cumene and chlorobenzene (Table II) do not suggest any induced decomposition or unusual mechanism changes at high

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(1) Compound, solvent, temperature, ΔV^* (cc/mole): AIBN,[2] toluene, 62.5°, +3.8; benzoyl peroxide,[3] CCl_4, 60°, +9.7; benzoyl peroxide,[4] styrene, 30°, +10; benzoyl peroxide,[5] acetophenone, 80°, +5; *t*-butyl peroxide[6] (DBPO), benzene, 120°, +13; DBPO,[6] CCl_4, 120°, +13; DBPO,[6] cyclohexene, 120°, +7; DBPO,[6] toluene, 120°, +5; pentaphenylethane,[2] toluene, 70°, +13.

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(10) Internal return in AIBN decomposition will be unlikely if N_2 is a primary decomposition product (*vide infra*).

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(13) Walling reasoned that the low values of ΔV^* for DBPO in cyclohexene and toluene reflected cage scavenging which prevented internal return.[6] Recently he has concluded that this is unlikely and that internal return probably occurs in these solvents.[9]

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(17) In this case, ΔV_1^* grossly represents two breaking bonds and a probable decrease in the length of one C–O bond associated with incipient CO_2.

(18) (a) Compressibility data for cumene[18b] and chlorobenzene[18c] indicate no phase transition over our pressure ranges. Extreme care was taken to correct for nonequilibrium conditions during pressure generation. Volumes of activation, at best, are tenuous numbers; however, the closeness of these values to zero precludes substantial absolute errors. (b) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, 77, 129 (1949); reprinted in "Collected Experimental Papers of P. W. Bridgman," Vol. VI, Harvard University Press, Cambridge, Mass., 1950, pp 3915–3932. (c) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **61**, 57 (1926); reprinted in "Collected Experimental Papers of P. W. Bridgman," Vol. IV, Harvard University Press, Cambridge, Mass., 1960, pp 2043–2086.