7140 *J. Am. Chem. Soc.* **1981**, *103*, 7140-7147

specificity. For example, the reaction of fluoride with neopentyl nitrite proceeds exclusively by the $E_{CO}2$ pathway, which is 60 kcal/mol less exothermic than the S_N2 reaction channel. The high selectivity in this reaction is further illustrated by a k_H/k_D isotope effect of about 2. These results provide important data on the relative barrier heights for these reactions in the double-well potential model described by Brauman and co-workers. Thus a coupling of organic probes with kinetic data can be useful in the detailed description of the potential energy surfaces which determine the course of the reaction.

The reactions of most carbanions with alkyl nitrites suggest the initial formation of an intermediate reaction complex in which the components are bound for periods long enough to permit one or more rearrangements. Many of the reactions can be explained in terms of simple organic mechanisms which have been well characterized in solution. A comprehensive mechanism for the reactions of carbanions with neopentyl nitrite involves nitrosation followed by proton transfer (path a) or nucleophilic attack on the carbonyl moiety (path b). In several cases fragmentation of the nitroso anion from path a can occur to generate a carboxylate ion (path c). These reactions generate a host of new and interesting species and can allow for the differentiation of isomeric reactant ions.

Finally, the strong gas-phase bases NH_2^- and OH^- react rapidly with most alkyl nitrites to form exclusively NO_2^- by mechanisms analogous to those discussed above. The reaction of amide with neopentyl nitrite generates the interesting product HN_2O^-.[28]

A comparison of flowing afterglow and ion cyclotron resonance results for the reactions of negative ions with alkyl nitrites identifies a few striking contrasts. An understanding of the origin of these differences may provide fundamental information about the nature of the potential energy surfaces on which gas-phase ion-molecule reactions occur.

Acknowledgment. We gratefully acknowledge support of this work by the U.S. Army Research Office.

Nucleophile Competition in Aromatic $S_{RN}1$ Reactions. Evaluation of Nucleophilic Reactivities and Evidence of Reaction Mechanism[1a]

Carlo Galli[1b] and Joseph F. Bunnett*

Contribution from the University of California, Santa Cruz, California 95064.
Received April 10, 1981

Abstract: Pairs of nucleophiles were allowed to react in ammonia with single substrates, mostly under irradiation, and relative nucleophilicities were evaluated from product yields. The $(EtO)_2PO^-$/pinacolone enolate ion reactivity ratio is 1.37 ± 0.11 with six substrates, PhI, PhBr, PhCl, PhF, Ph_2S, and $PhNMe_3^+I^-$. The constancy of this ratio is consistent with the $S_{RN}1$ mechanism but not with a conceivable alternative dubbed $S_{RN}2$. Three other nucleophiles were studied in pairwise competition with each of the original two. The five have the following relative reactivity: Ph_2P^-, 5.9 > Ph_2PO^-, 2.7 > $(EtO)_2PO^-$, 1.4 > $Me_3CCOCH_2^-$, (1.00) > PhS^-, 0.08. These and literature data show that, except for the obvious special case of PhS^-, nucleophile reactivities differ in aromatic $S_{RN}1$ reactions by not more than a factor of 10. The reason is possibly that the combination of aryl radical with nucleophile occurs virtually at encounter-controlled rate. *tert*-Butoxide ion (t-BuO$^-$), present in most experiments, has undetectably low nucleophilic reactivity vs. phenyl radical. The probable reason is that a σ^* radical anion, $[t\text{-BuOPh}]^{-\cdot}$, would be the initial product of combination of Ph· with t-BuO$^-$, and that it is energetically inaccessible because of the high energy level of the σ^* orbital of the aryl-oxygen bond.

The $S_{RN}1$ mechanism is a radical-chain mechanism of nucleophilic substitution.[2] It is well-supported by good evidence[2,3] but much of the evidence is indirect in the sense that the postulated intermediates have not been directly observed. Also, there are few quantitative data on reactivity.

Heretofore there has been little attention to competition between two nucleophiles reacting with a single substrate in $S_{RN}1$ systems.[1c] Studies of such competition can be doubly valuable, first because they probe the mechanism itself, and second for the information they provide about nucleophilic reactivities.

The propagation steps for $S_{RN}1$ reactions of one aromatic substrate (ArX) with two nucleophiles, Y^- and Z^-, are shown in Scheme I.

Scheme I

$$[ArX]^{-\cdot} \rightarrow Ar\cdot + X^- \tag{M1}$$

$$Ar\cdot + Y^- \rightarrow [ArY]^{-\cdot} \tag{M2y}$$

$$Ar\cdot + Z^- \rightarrow [ArZ]^{-\cdot} \tag{M2z}$$

$$[ArY]^{-\cdot} + ArX \rightarrow ArY + [ArX]^{-\cdot} \tag{M3y}$$

$$[ArZ]^{-\cdot} + ArX \rightarrow ArZ + [ArX]^{-\cdot} \tag{M3z}$$

According to this mechanism, nucleophiles participate in steps leading to their incorporation into reaction products chiefly in steps M2y and M2z. If the chain is long, that is, if propagation events are much more frequent than termination events, or if the termination steps do not form bonds between the aryl and nucleophile moieties, the relative yields of ArY and ArZ should, when account is also taken of the nucleophile concentrations, be indicative of the relative rate constants for steps M2y and M2z. Moreover, if the mechanism is correctly represented in Scheme I, if it is truly an aryl radical, from which nucleofugal group X has been separated, that interacts with the nucleophiles, the relative reactivity of two nucleophiles should be independent of the leaving group.

---

(1) (a) This research was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society. (b) Grateful recipient of a NATO Fellowship awarded by the Consiglio Nazionale delle Ricerche d'Italia. (c) The present work was presented in part in a preliminary communication: Galli, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 6137.

(2) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

(3) Saveant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323.

An alternative propagation cycle that has occasionally been suggested in informal conversations is presented, for the case of two competing nucleophiles, in Scheme II. We call this the $S_{RN}2$ mechanistic possibility,[4] for it has the same kind of relationship to $S_{RN}1$ as the S_N2 mechanism has to the S_N1. Its characteristic feature is that the nucleophile effects direct displacement of the nucleofugal group from radical anion $[ArX]^{-}\cdot$. Electron-transfer steps M3y and M3z are common to both alternatives. One can argue against the $S_{RN}2$ mechanism both on Coulombic and quantum mechanical grounds, but experimental evidence would be more compelling.

Scheme II

$$[ArX]^{-}\cdot + Y^{-} \rightarrow [ArY]^{-}\cdot + X^{-} \qquad (M4y)$$

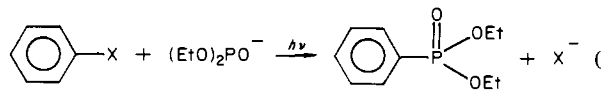
$$[ArX]^{-}\cdot + Z^{-} \rightarrow [ArZ]^{-}\cdot + X^{-} \qquad (M4z)$$

$$[ArY]^{-}\cdot + ArX \rightarrow ArY + [ArX]^{-}\cdot \qquad (M3y)$$

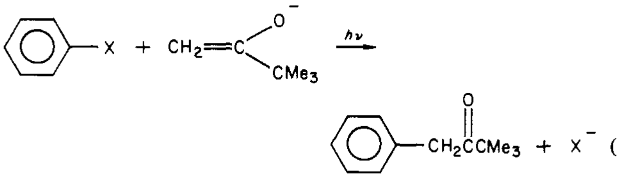
$$[ArZ]^{-}\cdot + ArX \rightarrow ArZ + [ArX]^{-}\cdot \qquad (M3z)$$

According to the $S_{RN}2$ mechanism, the relative reactivity of two nucleophiles ought to depend on the identity of leaving group X. Especially if the two nucleophiles are of different character, for example, having nucleophilic sites representing different elements, the energies of the two transition states should depend on the specific characteristics of the entering and leaving groups, as is the case with S_N2 and S_NAr processes. Even if steps M4y and M4z occurred at encounter-controlled rates, some selection between nucleophiles of different steric characteristics should occur as the size of the leaving group varied.

An experimental test of mechanism is thus indicated. For a series of substrates with a common aryl group but differing leaving groups, the relative reactivity of two nucleophiles of rather different character should be constant for the $S_{RN}1$ mechanism but variable and dependent on the leaving group for the $S_{RN}2$. We have conducted such a test, utilizing as nucleophiles diethyl phosphite ion[5-7] and pinacolone enolate ion,[8,9] both of which are known to react satisfactorily with phenyl halides according to eq 1 and 2, and as substrates the four phenyl halides plus diphenyl sulfide and phenyltrimethylammonium ion.

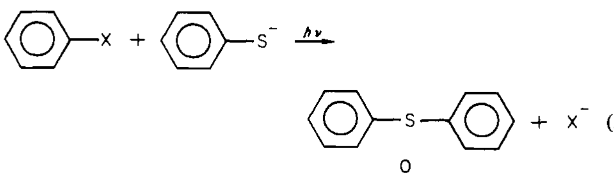


(1)

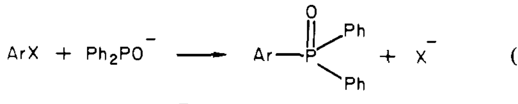


(2)

Also, we have extended our study to include three further nucleophiles, chiefly in reaction with iodobenzene or *p*-iodotoluene. They react[10-12] as indicated in eq 3-5.



(3)



(4)

$$ArX + Ph_2P^{-} \longrightarrow ArPPh_2 + X^{-} \qquad (5)$$

Results

In a typical competition experiment, an ammonia solution of the aryl halide or other substrate (usually 0.01–0.05 M) and the two competing nucleophiles, each in two- to threefold excess over the substrate, under an atmosphere of dinitrogen, was either exposed to the radiation from fluorescent lamps emitting maximally at 350 nm or allowed to react in the dark. At measured times, samples were quenched with aqueous ammonium nitrate, and organic products such as indicated in eq 1–5 were determined by GLC. Relative nucleophile reactivities were reckoned on the assumption that the reaction of each nucleophile with the reactive intermediate was kinetically first order in nucleophile.[13] Our principal experiments are summarized in Table I.

Competition between Diethyl Phosphite Ion and Pinacolone Enolate Ion. Attention is called to experiments 1–12, Table I. One noteworthy feature of them was the occurrence of a small amount of diphenylation of pinacolone enolate ion, to form $Ph_2CHCOCMe_3$, usually to the extent of about 9% of the $PhCH_2COCMe_3$ produced.[8] In reckoning the reactivity of pinacolone enolate ion, we combined the yields of the diphenyl and monophenyl derivatives of pinacolone. Also noteworthy is that diethyl phenylphosphonate (cf. eq 1) is gradually consumed in the reaction mixtures involved. We showed independently that $PhPO(OEt)_2$ is slowly destroyed (to a noticeable extent after 15 min; see Experimental Section) on reaction with pinacolone enolate ion, probably by S_N2 attack at C-1 of an ethyl group. Accordingly no data at times longer than 480 s were used to evaluate the relative reactivities of these two nucleophiles, except in the case of fluorobenzene. Fluorobenzene reacts so slowly (experiments 9 and 10) that reactions had to be conducted for longer times in order to generate products in quantities sufficient to be convincing; the apparent reactivity of $(EtO)_2PO^{-}$ with respect to the enolate ion diminished with time, but extrapolation back to zero time gave an estimate of the true reactivity ratio.

Although there is some variation in the calculated ratio of the reactivity of diethyl phosphite ion with respect to pinacolone enolate ion, it is not significantly different between samples from the same experiment, or between different experiments with the same substrate, or between substrates. Furthermore, minor differences in the irradiation provided have no significant effect on the reactivity ratio; it is essentially the same whether 16 lamps emitting maximally at 300 nm are used in the photochemical reactor (experiment 6), or one "350 nm" lamp (experiments 1, 5, and 8), or 16 "350 nm" lamps (the other experiments).

In Table II, the mean values of the relative reactivity of diethyl phosphite ion vs. pinacolone enolate ion are listed, substrate by substrate. The mean value for the six substrates, PhI, PhBr, PhCl, PhF, Ph_2S, and $PhNMe_3^{+}$, is 1.37 ± 0.11.

The Reactivity of Thiophenoxide Ion. A potential complication in competition of this nucleophile with pinacolone enolate ion is that diphenyl sulfide, the product of thiophenoxydehalogenation (eq 3), can itself effect $S_{RN}1$ phenylation of a ketone enolate ion.[14] Accordingly only iodobenzene, the most reactive of the halobenzenes, was used as substrate, in experiment 13. The fact that the apparent reactivity of PhS^{-} as compared to pinacolone enolate ion did not diminish with time suggests that the potential complication did not seriously affect the results obtained. The mean estimate of the PhS^{-} relative reactivity is 0.079 (Table II).

The relative reactivity of thiophenoxide ion with respect to diethyl phosphite ion was determined, in experiments 22 and 23, to be on average 0.061 (Table II). Again because of the possibility that Ph_2S might be consumed in phenylation of the competing nucleophile, iodobenzene was used as substrate. Multiplication of 0.061 by 1.37, which is the relative reactivity of diethyl phosphite ion vs. pinacolone enolate ion, gives 0.084 as the estimated reactivity of PhS^{-} vs. the enolate ion. This value obtained via the

---

[4] Rather confusingly, the symbol "$S_{RN}2$" was applied, after the appearance of our preliminary communication,[1c] to a mechanistic hypothesis of wholly different character, see: Katritzky, A. R.; de Ville, G. Z.; Patel, R. C. *Tetrahedron Lett.* **1980**, 1723.

[5] Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3612.

[6] Hoz, S.; Bunnett, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 4690.

[7] Bunnett, J. F.; Traber, R. P. *J. Org. Chem.* **1978**, *43*, 1867.

[8] Bunnett, J. F.; Sundberg, J. E. *J. Org. Chem.* **1976**, *41*, 1702.

[9] Scamehorn, R. G.; Bunnett, J. F. *J. Org. Chem.* **1977**, *42*, 1449.

[10] Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173.

[11] Swartz, J. E.; Bunnett, J. F. *J. Org. Chem.* **1979**, *44*, 4673.

[12] Swartz, J. E.; Bunnett, J. F. *J. Org. Chem.* **1979**, *44*, 340.

[13] Bunnett, J. F. In "Investigation of Rates and Mechanisms of Reactions", 3rd ed.; Lewis, E. S., Ed.; Wiley-Interscience: New York, 1974; Part I, p 159.

[14] Rossi, R. A.; Bunnett, J. F. *J. Org. Chem.* **1973**, *38*, 1407.

Table I. Competition Experiments, Each with One Substrate and Two Nucleophiles,[a] in Ammonia at Reflux

	substrate[b]		nucleophile Y^-		nucleophile Z^-					
expt no.	identity	concn, M	identity	concn, M	identity	concn, M	irradiation time,[c] s	ArY, %	ArZ, %	k_{Y^-}/k_{Z^-}
1	PhI	0.052	$(EtO)_2PO^-$	0.127	*t*-$BuCOCH_2^-$	0.157	30^d	10.2	9.3^e	1.56
							90^d	22.2	18.7^e	1.37
							150^d	34.5	30.3^e	1.33
							300^d	45.1	40.8^e	1.30
2	PhI	0.050	$(EtO)_2PO^-$	0.106	*t*-$BuCOCH_2^-$	0.100	11	25.5	16.4^e	1.39
							33	52.9	36.5^e	1.37
							70	56.3	40.1^e	1.35
3	PhI	0.055	$(EtO)_2PO^-$	0.119	*t*-$BuCOCH_2^-$	0.113	9	19.0	12.8^e	1.31
							18	33.7	22.3^e	1.34
							27	45.6	32.3^e	1.25
4	PhBr	0.052	$(EtO)_2PO^-$	0.114	*t*-$BuCOCH_2^-$	0.143	30	14.0	13.0^e	1.52
							75	33.0	29.6^e	1.32
5	PhBr	0.055	$(EtO)_2PO^-$	0.122	*t*-$BuCOCH_2^-$	0.146	225^d	13.0	9.0^e	1.61
							480^d	20.0	16.0^e	1.41
6	PhBr	0.056	$(EtO)_2PO^-$	0.117	*t*-$BuCOCH_2^-$	0.139	20^f	2.4	1.7^e	1.52
							42^f	8.7	7.1^e	1.35
							80^f	17.4	15.6^e	1.27
							210^f	34.8	33.4^e	1.19
							480^f	49.8	46.8^e	1.20
7	PhCl	0.070	$(EtO)_2PO^-$	0.119	*t*-$BuCOCH_2^-$	0.139	40	9.1	5.3^e	1.85
							90	14.4	10.6^e	1.47
							180	24.7	17.4^e	1.54
							390	42.6	28.8^e	1.64
8	PhCl	0.049	$(EtO)_2PO^-$	0.123	*t*-$BuCOCH_2^-$	0.137	140^d	2.7	2.0^e	1.37
							360^d	6.4	4.9^e	1.33
9	PhF	0.051	$(EtO)_2PO^-$	0.122	*t*-$BuCOCH_2^-$	0.147	400	1.8	1.6^e	1.32
10	PhF	0.046	$(EtO)_2PO^-$	0.123	*t*-$BuCOCH_2^-$	0.143	600	2.7	2.7^e	1.16
							1200	3.5	4.6^e	0.96
							3660	6.5	11.5^e	0.56
11	Ph_2S	0.047	$(EtO)_2PO^-$	0.123	*t*-$BuCOCH_2^-$	0.141	30	4.4	3.3^e	1.41
							60	12.0	8.5^e	1.49
							180	36.0	26.2^e	1.49
12	$PhNMe_3^+I^-$	0.051	$(EtO)_2PO^-$	0.122	*t*-$BuCOCH_2^-$	0.146	25	11.4	10.4^e	1.23
							60	26.0	22.6^e	1.30
							60	26.0	24.1^e	1.22
							140	41.3	38.6^e	1.23
13	PhI	0.051	PhS^-	0.197	*t*-$BuCOCH_2^-$	0.082	30	4.2	20.1^e	0.076
							50	9.0	35.1^e	0.088
							90	12.5	54.4^e	0.074
							180	18.5	69.7^e	0.079
14	PhI	0.049	Ph_2PO^- [g]	0.118	*t*-$BuCOCH_2^-$	0.138	10	15.0^h	5.5^e	2.84
							25	24.9^h	14.0^e	1.97
							65	54.2^h	29.5^e	2.23
							480	60.8^h	32.3^e	2.33
15	PhI	0.046	Ph_2PO^- [g]	0.095	*t*-$BuCOCH_2^-$	0.113	(60)^c	4.3^h	1.2	2.51
							(300)^c	9.6^h	3.3	2.83
							(1800)^c	28.4^h	12.0	2.77
							(7800)^c	38.8^h	21.6	2.16
16	PhI	0.054	Ph_2P^-	0.118	*t*-$BuCOCH_2^-$	0.132	(300)^c	28.0	4.6	7.38
							(810)^c	38.0	8.6	5.34
							(1560)^c	48.0	11.5	5.15
							(3480)^c	64.7	16.2	5.09
17	*p*-TolI	0.013	Ph_2P^-	0.037	*t*-$BuCOCH_2^-$	0.034	(300)^c	47.9	6.0^e	7.20
							(600)^c	56.4	8.5^e	6.17
							(1500)^c	75.6	14.4^e	5.03
							(3360)^c	87.6	15.8^e	5.45
18	*p*-TolI	0.013	Ph_2P^-	0.038	*t*-$BuCOCH_2^-$	0.032	15	30.3	3.7^e	6.77
							40	58.7	9.5^e	5.29
							74	74.4	12.1^e	5.43
							130	77.5	13.0^e	5.29
19	*p*-TolBr	0.012	Ph_2P^-	0.038	*t*-$BuCOCH_2^-$	0.033	(9000)^c	3.04	0.095	27.4
							(16200)^c	9.1	0.3	26.2
20	*p*-TolBr	0.012	Ph_2P^-	0.038	*t*-$BuCOCH_2^-$	0.033	420	16.1	2.0	7.23
							840	25.6	3.8	6.06
							1500	31.4	5.5	5.21
21	PhCl	0.013	Ph_2P^-	0.036	*t*$BuCOCH_2^-$	0.034	3060	9.6	1.06	8.7
							6900	28.6	2.6	11.0
							16200	50.5	4.9	10.7
22	PhI	0.045	PhS^-	0.141	$(EtO)_2PO^-$	0.072	45	10.8	67.5	0.065
							80	12.0	86.8	0.050
23	PhI	0.045	PhS^-	0.124	$(EtO)_2PO^-$	0.091	15	3.7	39.2	0.063
							25	6.1	58.4	0.067
							35	8.4	80.6	0.062

Table I (*Continued*)

	substrate[b]		nucleophile Y^-		nucleophile Z^-					
expt no.	identity	concn, M	identity	concn, M	identity	concn, M	irradiation time,[c] s	ArY, %	ArZ, %	k_{Y^-}/k_{Z^-}
24	PhI	0.052	Ph_2PO^- [g]	0.098	$(EtO)_2PO^-$	0.148	11	2.1[h]	0.7	2.49
							25	2.5[h]	1.4	1.83
							55	5.5[h]	3.4	2.06
							240	27.4[h]	17.4	2.40
							1200	47.1[h]	32.5	2.32
25	*p*-TolI	0.047	Ph_2PO^- [g]	0.047	$(EtO)_2PO^-$	0.147	60	6.9	2.5	4.17
							180	14.5	11.2	1.99
							480	35.0	24.3	2.29
							900	52.6	39.3	2.18
26	*p*-TolI	0.013	Ph_2P^-	0.035	$(EtO)_2PO^-$	0.033	(120)[c]	19.3	4.1	4.55
							(300)[c]	39.3	8.6	4.58
							(720)[c]	53.0	12.4	4.39
27	*p*-TolI	0.040	Ph_2P^-	0.022	$(EtO)_2PO^-$	0.203	(270)[c]	8.3	19.3	4.26
							(480)[c]	11.7	28.4	4.18
28	PhBr	0.013	Ph_2P^-	0.036	$(EtO)_2PO^-$	0.033	630	26.2	1.7	15.4
							1230	55.9	3.5	16.1

[a] All nucleophiles as potassium salts. [b] "*p*-Tol" stands for *p*-tolyl. [c] Parentheses indicate reaction in the dark. [d] One "350 nm" lamp in the photochemical reactor. [e] Accompanied by $Ph_2CHCOCMe_3$, about 9% of the amount of $PhCH_2COCMe_3$ formed. [f] Sixteen "300 nm" lamps in the photochemical reactor. [g] The Ph_2PHO used was contaminated with 0.9% of Ph_3PO. [h] Ph_3P was determined as Ph_3PO; the yield of Ph_3PO was corrected for the small amount of Ph_3PO contaminating the Ph_2PO^- reagent before the reactivity ratio was calculated.

Table II. Mean Values of Nucleophile Reactivities Relative to Pinacolone Enolate Ion and Diethyl Phosphite Ion

				relative reactivity		
substrate	nucleophile	illumination	exceptions	vs. $t\text{-}BuCOCH_2^-$	vs. $(EtO)_2PO^-$	vs. $t\text{-}BuCOCH_2^-$ via relay
PhI	$(EtO)_2PO^-$	yes	*a*	1.33 ± 0.04		
PhBr	$(EtO)_2PO^-$	yes		1.38 ± 0.15		
PhCl	$(EtO)_2PO^-$	yes	*b*	1.47 ± 0.13		
PhF	$(EtO)_2PO^-$	yes	*c*	1.38 ± 0.10		
Ph_2S	$(EtO)_2PO^-$	yes		1.46 ± 0.05		
$PhNMe_3^+I^-$	$(EtO)_2PO^-$	yes		1.25 ± 0.04		
five PhX[d]	$(EtO)_2PO^-$	yes	*a, b*	1.37 ± 0.12		
six PhX[e]	$(EtO)_2PO^-$	yes	*a, b*	1.37 ± 0.11		
PhI	PhS^-	yes		0.079 ± 0.006		
PhI	Ph_2PO^-	yes		2.34 ± 0.36		
PhI	Ph_2PO^-	dark		2.57 ± 0.31		
PhI	Ph_2P^-	dark	*f*	5.19 ± 0.13		
p-TolI	Ph_2P^-	dark		5.96 ± 0.95		
p-TolI	Ph_2P^-	yes		5.70 ± 0.72		
p-TolBr	Ph_2P^-	dark		26.8 ± 0.6		
p-TolBr	Ph_2P^-	yes		6.17 ± 1.01		
PhCl	Ph_2P^-	yes		10.1 ± 1.3		
PhI	PhS^-	yes			0.061 ± 0.007	0.084 ± 0.16
PhI	Ph_2PO^-	yes			2.20 ± 0.31	3.02 ± 0.66
p-TolI	Ph_2PO^-	yes	*g*		2.15 ± 0.15	2.95 ± 0.44
p-TolI	Ph_2P^-	dark			4.39 ± 0.18	6.02 ± 0.73
PhBr	Ph_2P^-	yes			15.8 ± 0.4	

[a] Experiment 1, 30 s. [b] Experiment 7, 40 s. [c] Relative reactivity estimated by linear regression extrapolation to zero time is 1.46 on the basis of experiment 9 and the first two samples from experiment 10 but 1.31 if the 3660 s sample from experiment 10 is also taken into account; the average is 1.38 ± 0.10 (uncertainty estimated intuitively). [d] Data for PhI, PhBr, PhCl, Ph_2S, and $PhNMe_3^+I^-$. [e] Data for the foregoing five plus 1.38 for PhF, entered four times. [f] Experiment 16, 300 s. [g] Experiment 25, 60 s.

diethyl phosphite ion relay agrees well with 0.079 as determined by direct comparison.

The Reactivity of Diphenylphosphinite Ion. This ion, Ph_2PO^-, reacts readily with aryl iodides under photostimulation[11]; see eq 4. In experiment 14, Table I, its relative reactivity vs. pinacolone enolate ion is shown to be 2.34. The same two nucleophiles also react with iodobenzene in the dark (experiment 15), albeit more slowly, and the estimated reactivity ratio of 2.57 is not significantly different from that under irradiation (Table II).

Diphenylphosphinite ion was also pitted against diethyl phosphite ion. In experiment 24, Table I, iodobenzene was the substrate, and the average reactivity of Ph_2PO^- vs. $(EtO)_2PO^-$ is 2.20. Multiplication by 1.37 gives 3.02 as the relative reactivity of Ph_2PO^- with respect to pinacolone enolate ion. This estimate is, within experimental error, indistinguishable from that measured by direct comparison.

Competition between Ph_2PO^- and $(EtO)_2PO^-$ was also carried out with *p*-iodotoluene as substrate (experiment 25). The purpose of doing so was to gain absolute freedom from an uncertainty that attended reactions with iodobenzene stemming from the presence of a minor impurity of Ph_3PO in the Ph_2PHO used to prepare the Ph_2PO^- reagent. Triphenylphosphine oxide formed during the competition experiment was indistinguishable from that carried through as a contaminant, and we were obliged to apply a correction (in experiments 14, 15, and 24) for the contaminant. Using *p*-iodotoluene as substrate provided an escape from the contamination problem inasmuch as $p\text{-}CH_3C_6H_4POPh_2$ has a different GLC retention time than Ph_3PO. In experiment 25, the average reactivity of Ph_2PO^- vs. $(EtO)_2PO^-$ was 2.15 (as listed in Table II, third line from the end), essentially the same as in experiments with iodobenzene as substrate.

The Reactivity of Diphenylphosphide Ion. This ion undergoes facile $S_{RN}1$ reaction with aryl iodides (cf. eq 5), even in the dark, but faster under irradiation.[12] When it was placed in competition with pinacolone enolate ion, its relative reactivity in the dark with iodobenzene substrate (experiment 16) was 5.2, in the dark with *p*-iodotoluene substrate (experiment 17) 6.0, and under irradiation with the latter substrate (experiment 18) 5.7; these are the same within experimental error. Likewise, with *p*-bromotoluene under irradiation (experiment 20), this reactivity ratio was 6.2. However, with *p*-bromotoluene in the dark, the greatly deviant ratio of 26.8 was indicated (experiment 19). Also deviant was the apparent diphenylphosphide ion/pinacolone enolate ion rate ratio with chlorobenzene under illumination, namely, 10.1 (experiment 21). If these last two deviant ratios are neglected, the average value of this rate ratio (from experiments 16, 17, 18, and 20) is 5.8 ± 0.8.

Experiments pitting Ph_2P^- against $(EtO)_2PO^-$ also gave contrasting results. With substrate *p*-iodotoluene in the dark (experiments 26 and 27), the reactivity ratio $Ph_2P^-/(EtO)_2PO^-$ was 4.39 ± 0.18; multiplication by 1.37 gives 6.0 ± 0.7 as the reactivity of diphenylphosphide ion, relative to pinacolone enolate ion, via the diethyl phosphite ion relay. This agrees excellently with the reactivity measured directly in experiments 16–18 and 20. However, with PhBr under irradiation (experiment 28), the apparent $Ph_2P^-/(EtO)_2PO^-$ ratio was 15.8.

Nucleophilic Reactivity Summary. Except for the deviant results from experiments 19, 21, and 28, our results fall into a consistent and reproducible order of nucleophile reactivity, as follows: Ph_2P^-, 5.9 > Ph_2PO^-, 2.7 > $(EtO)_2PO^-$, 1.4 > $Me_3CCOCH_2^-$, (1.00) > PhS^-, 0.08.

Discussion

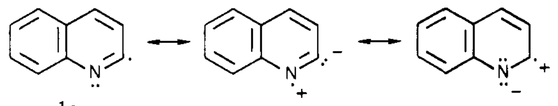
On the $S_{RN}1$ vs. $S_{RN}2$ Question. As stated in the introduction, with reference to Scheme I, the relative reactivities of nucleophiles in $S_{RN}1$ reactions should be independent of the leaving group because the leaving group has left at the point on the propagation cycle at which the aryl radical interacts with the nucleophile or nucleophiles. Our measurements (Table I), apart from the deviant outcomes of experiments 19, 21 and 28, show relative nucleophilic reactivity to be independent of the leaving group.

As also stated above, relative nucleophile reactivity according to the $S_{RN}2$ mechanistic model should depend on the leaving group. In other reaction systems in which the nucleofugal group is present while the nucleophile attacks, relative nucleophile reactivity is significantly or strongly dependent on the leaving group. Thus, in S_NAr reactions with 1-halo-2,4-dinitrobenzenes, the PhS^-/MeO^- rate ratio varies from 59 with fluoride nucleofuge to 16 800 when iodine is the leading group, and the piperidine/MeO^- rate ratio varies from 0.85 to 1.48 for the same change of substrates.[15] In reactions with 2-halothiazoles, the PhS^-/MeO^- ratio inverts from 0.007 to 27 as the nucleofugal group changes from fluorine to iodine.[16] In S_N2 reactions of lithium halides with alkyl halides, the I^-/Br^- rate ratio changes from 1.2 to 4.0, and the Br^-/Cl^- ratio from 17 to 36, as the substrate changes from EtBr to EtI.[15] Even when the nucleophiles are as similar as phenoxide ion and *p*-nitrophenoxide ion and the substrates are restricted to methyl esters of sulfonic acids, relative nucleophilic reactivity in S_N2 displacements has been observed to vary nearly threefold as the sulfonate leaving group changes.[17] It should be noted that in the S_NAr reactions cited, the nucleofugal group affects the relative rates of attack by different nucleophiles even though the bond to it is not sundered in the rate-limiting step.

One might argue that the steps in which the nucleophiles interact with the $[ArX]^{-\cdot}$ occurred at encounter-controlled rates that were unaffected by the identity of the nucleofugal group. In that case, however, there should nevertheless be some rate differentiation among nucleophiles of different steric requirements, such as diethyl phosphite and pinacolone enolate ions, stemming from the different bulk of the nucleofugal groups. It is instructive that rate constants for the encounter-controlled reactions of the hydrated proton with several $RCOO^-$ vary considerably as R is varied: $HCOO^-$, 5.0; CH_3COO^-, 4.5; $CH_3CH_2COO^-$, 4.3; Me_3CCOO^-, 1.53 (all × 10^{10} M^{-1} s^{-1}).[18] In our study, fluorine is a very small and trimethylammonio quite a large nucleofugal group; the fact that the observed selectivity among the two nucleophiles is the same for PhF and $PhNMe_3^+$ is incompatible with the $S_{RN}2$ mechanism even for the hypothetical case in which steps M4y and M4z (Scheme II) occur at encounter-controlled rates.

Comparison with Other Data Concerning the Same Nucleophiles. Recently Amatore, Chaussard, Pinson, Saveant, and Thiebault[19] have estimated, by analysis of electrochemical data, rate constants for the combination of the 2-quinolyl radical (**1**) with some of the nucleophiles of the present study, in liquid ammonia at −40 °C. The reported values are: acetone enolate ion, 7.5×10^6 M^{-1} s^{-1}; PhS^-, 1.4×10^7 M^{-1} s^{-1}; $(EtO)_2PO^-$, 1.8×10^7 M^{-1} s^{-1}. Relative reactivities are: acetone enolate ion, (1.0); PhS^-, 1.9; and $(EtO)_2PO^-$, 2.4. If acetone and pinacolone enolate ions have nearly the same reactivity, as indeed one study shows they do,[20] the relative reactivity estimated by Amatore et al. for $(EtO)_2PO^-$ (2.4) is fairly close to that which we measured (1.4). However, they report thiophenoxide ion to have relative reactivity about 24 times greater than our data indicate.

In comparing our data and theirs, one must bear in mind that different radicals are involved in the two studies. Although one might expect the phenyl and 2-quinolyl radicals to be similarly selective between nucleophiles, it is not required in principle that they should be. In this connection, it should be noted that the 2-quinolyl radical presents a possibility for spin delocalization (**1a** ⇌ **1b**) that is unavailable to the phenyl radical. Such delocalization might affect selectivity between nucleophiles, as well as absolute reactivity. As to the effects of resonance on the electrical charge at C-2, structures **1b** and **1c** would make opposite contributions of uncertain relative magnitudes.



1a 1b 1c

Significance of the Small Spread in Nucleophilic Reactivity. With the exception of thiophenoxide ion, the nucleophilicities of the nucleophiles studied are of similar magnitude; the extreme variation is only sixfold. Other measurements of relative nucleophilicity in aromatic $S_{RN}1$ reactions also show remarkably little dependence of rate on the identity of the nucleophile. Thus, in reactions provoked by solvated electrons, amide ion (NH_2^-) is 2.0 times as reactive as acetone enolate ion vs. the 2,4,6-trimethylphenyl radical[21] and 1.9 times as reactive vs. the phenyl radical.[22] Versus phenyl radical in Me_2SO solution, the enolate ion from acetone is slightly more reactive than that from pinacolone and 1.4 times as reactive as that from cyclohexanone.[20] Versus phenyl radical in ammonia, the cyanomethyl anion exceeds acetone enolate ion in reactivity by about sixfold (in the experiment most suitable for estimation of relative reactivity).[23]

These bits of information from here and there,[24] together with our own results, show quite a number of nucleophiles of diverse chemical type to differ in nucleophilic reactivity toward aryl radicals by something like tenfold at most, except for PhS^-. Why does relative reactivity fall within such a narrow range? One possibility is that the reaction of an aryl radical with a nucleophile occurs, within this set of nucleophiles, virtually at encounter-controlled rate.[12,27] Evidence independently suggesting such a

---

(15) Bunnett, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 5969.

(16) Bartoli, G.; Todesco, P. E. *Acc. Chem. Res.* **1977**, *10*, 125.

(17) Lewis, E. S.; Vanderpool, S. *J. Am. Chem. Soc.* **1977**, *99*, 1946.

(18) Crooks, J. E. In "Comprehensive Chemical Kinetics", Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1977; Vol. 8, pp 220–1.

(19) Amatore, C.; Chaussard, J.; Pinson, J.; Saveant, J.-M.; Thiebault, A. *J. Am. Chem. Soc.* **1979**, *101*, 6012.

(20) Scamehorn, R. G.; Hardacre, J., results privately communicated.

(21) Tremelling, M. J.; Bunnett, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 7375.

(22) Bunnett, J. F.; Gloor, B. F., quoted in ref 21.

(23) Bunnett, J. F.; Gloor, B. F. *J. Org. Chem.* **1973**, *38*, 4156.

(24) Enolate ion relative reactivities have also been measured in $S_{RN}1$ reactions involving heteroaryl radical intermediates. The enolate ion from 2,4-dimethyl-3-pentanone is 3.2 times as reactive as that from acetone vs. 2-quinolyl radical[25] and 3.7 times as reactive vs. 2-pyridyl radical.[26]

(25) Hay, J. V.; Wolfe, J. F. *J. Am. Chem. Soc.* **1975**, *97*, 3702.

(26) Komin, A. P.; Wolfe, J. F. *J. Org. Chem.* **1977**, *42*, 2481.

(27) The rate constants reported by Amatore et al.[19] for reactions of 2-quinolyl radical, quoted above, are significantly below the encounter-controlled limit. Possibly the condition of delocalization, **1a** ⇌ **1b**, which should stabilize the radical, reduces its reactivity by as much as two powers of 10.

state of affairs is that the photostimulated reaction of iodobenzene with diethyl phosphite ion is but little affected by dioxygen or by the presence of $(EtO)_2PHO$;[6] for the reactions of these species with phenyl radical, rate constants of 4.6×10^9 and 1.05×10^7 $M^{-1}\ s^{-1}$, respectively, have been estimated.[28]

As for thiophenoxide ion, the product of its combination with phenyl radical, the diphenyl sulfide radical anion, is known[14] to fragment to form Ph· and PhS^-. Taking into account evidence that such fragmentation does not occur appreciably on the time scale of $S_{RN}1$ reactions of PhS^- with aryl halides to form diaryl sulfides,[29] we can exclude the possibility that fragmentation of $[Ph_2S]^{-}\cdot$ is the cause of the relatively low nucleophilic reactivity of PhS^- revealed by our measurements. It is probable that the encounter complex of Ph· with PhS^- (formed in step M5, Scheme III) dissociates to regenerate the species whence it arose faster than it undergoes carbon–sulfur bond formation (in step M6) to form diphenyl sulfide radical anion. In these circumstances the rate of combination of Ph· with PhS^- to form $[Ph_2S]^{-}\cdot$ would fall below the encounter-controlled limit.

Scheme III

$$\mathrm{Ph}\cdot + \mathrm{PhS}^- \rightleftarrows \overline{\mathrm{Ph}\cdot\ \mathrm{PhS}^-} \tag{M5}$$

$$\overline{\mathrm{Ph}\cdot\ \mathrm{PhS}^-} \rightarrow [\mathrm{Ph{-}S{-}Ph}]^{-}\cdot \tag{M6}$$

The Unreactivity of Oxyanion Nucleophiles. There is no confirmed example of the participation of an oxyanion nucleophile in an aromatic $S_{RN}1$ reaction to form an oxygen-arylated product.[30] In most of the reactions of the present study, excess potassium *tert*-butoxide was present but no phenyl *tert*-butyl ether was ever found as a product. No $S_{RN}1$ oxygen arylation of a ketone enolate ion has ever been detected. The unreactivity of oxyanion nucleophiles is remarkable in view of the high basicity of alkoxide ions and their prominence as nucleophiles in other types of processes.

Insight into the unreactivity of oxyanion nucleophiles comes from consideration of the orbitals utilized during combination of an aryl radical with a nucleophile. A central question is where the "extra" electron goes, that is, what orbital is used to accommodate it. The problem is simplified and sharpened if one restricts attention to nucleophiles that do not themselves provide a π system in which conceivably the "extra" electron might be accommodated; nucleophiles within this restricted group include alkanethiolate ions,[29,35] amide ion,[21,36] iodide ion,[37] and alkoxide ions.

Let us consider a phenyl radical interacting with, say, an amide ion. The phenyl radical has one electron in a carbon sp^2 orbital, the axis of which is in the plane of the benzene ring, and the amide ion has two electrons in a nitrogen orbital conveniently considered to be a 2p orbital. Conceivably as these two orbitals overlap to form a σ bond, the "extra" electron migrates from the sp^2 orbital into a π^* orbital of the benzene ring. However, the sp^2 orbital is orthogonal with the π^* orbitals, and a smooth and rapid transfer of an electron between the two orthogonal systems is improbable.

An alternative possibility is that the "extra" electron is accommodated in the σ^* orbital of the forming C–N bond. The immediate product of combination is a σ^* radical anion, the structure of which, in the notation of Asmus,[38] might be represented as **2**. The σ^* radical anion then more slowly changes, probably with assistance of bending vibrations to circumvent the orthogonality constraint, to the more stable π^* radical anion.

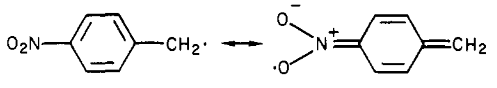
$$\mathrm{Ph}\cdot + \mathrm{NH_2}^- \rightarrow \underset{\mathbf{2}}{\mathrm{Ph}^{\cdot}.\mathrm{NH_2}^-}$$

The postulated process resembles the microscopic reverse of the mechanism suggested by Riederer, Hüttermann, and Symons,[39] on experimental grounds, for the fragmentation of aryl halide radical anions. They suggest that the π^* radical anion, normally the more stable, undergoes electron migration from the π^* to the σ^* orbital, and that it is the resulting σ^* radical anion that fragments.

One gains insight, according to this hypothesis, into why oxyanion nucleophiles are unreactive. Because of the high electronegativity of oxygen, the C–O σ (bonding) orbital is at a low energy and the normal C–O single bond is a strong one. However, the σ^* (antibonding) orbital is for the same reason at an exceptionally high energy level.[40] Accordingly, the combination of an aryl radical with an oxyanion nucleophile would involve formation of a σ^* radical anion at a very high energy level, a level inaccessibly high.

The electronegativity of nitrogen is less than that of oxygen. The difference is apparently enough to enable transitory utilization of the σ^* orbital of the C–N bond during combination of phenyl radical with amide ion.[41]

Oxyanion nucleophiles do occasionally combine with radicals of the *p*-nitrobenzyl type in the course of aliphatic $S_{RN}1$ reactions.[43,44] As Kronblum[45] has pointed out, with attention to canonical forms such as **3b**, such steps can be considered as Michael-like attachments of nucleophiles to unsaturated systems. The filled outer shell orbital of the nucleophile interacts with a π orbital at the benzylic radical site. This situation is of character fundamentally different from that when a nucleophile interacts with an aryl radical.



3a 3b

Comparison of Relative Nucleophilicities of Anions with Deelectronation Energies.[46] Brauman and co-workers[47] have determined deelectronation energies[46] of several anions in the gas phase by electron photodetachment spectroscopy. Some of their

---

(28) Kryger, R. G.; Lorand, J. P.; Stevens, N. R.; Herron, N. R. *J. Am. Chem. Soc.* **1977**, *99*, 7589.

(29) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1975**, *40*, 3740.

(30) It has been claimed[31] that halobenzenes react with phenoxide ion in aqueous *tert*-butyl alcohol under stimulation of solvated electrons contributed by sodium amalgam to form diphenyl ether, but an effort to confirm that experimental result could not do so.[32] In other studies, phenoxide ions have also been found to be ineffective as nucleophiles in aromatic $S_{RN}1$ reactions.[33,34]

(31) Rajan, S.; Sridaran, P. *Tetrahedron Lett.* **1977**, 2177.

(32) Rossi, R. A.; Pierini, A. B. *J. Org. Chem.* **1980**, *45*, 2914.

(33) Rossi, R. A.; Bunnett, J. F. *J. Org. Chem.*, **1973**, *38*, 3020.

(34) Semmelhack, M. F.; Bargar, T. *J. Am. Chem. Soc.* **1980**, *102*, 7765.

(35) Rossi, R. A.; Hoyos de Rossi, R.; Lopez, A. F. *J. Am. Chem. Soc.* **1976**, *98*, 1252.

(36) Kim, J. K.; Bunnett, J. F. *J. Am. Chem. Soc.* **1970**, *92*, 7463, 7464.

(37) Lawless, J. G.; Hawley, M. D. *J. Electroanal. Chem.* **1969**, *21*, 365.

(38) Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436.

(39) Riederer, H.; Hüttermann, J.; Symons, M. C. R. *Chem. Commun.* **1978**, 313.

(40) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976; pp 12–5.

(41) In his lecture to the Fifth IUPAC Conference on Physical Organic Chemistry, Santa Cruz, CA, August 19, 1980, Professor Symons spoke of his experimental evidence and his hypothesis that $\pi^*[ArX]^{-}\cdot$ fragment via σ^*-$[ArX]^{-}\cdot$ intermediates. In the ensuing discussion, one of us pointed out the relevance of his views to interpretation of mechanism and reactivity in reactions of nucleophiles with aryl radicals. We are pleased to see that these thoughts were included in the published version of the lecture.[42]

(42) Symons, M. C. R. *Pure Appl. Chem.* **1981**, *53*, 223.

(43) Kornblum, N. *Angew. Chem.* **1975**, *87*, 797; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.

(44) Norris, R. K.; Randles, D. *Aust. J. Chem.* **1976**, *29*, 2621.

(45) Kornblum, N.; Ackermann, P.; Swiger, R. T. *J. Org. Chem.* **1980**, *45*, 5294.

(46) Brauman and co-workers[47] speak of *electron photodetachment* energies of anions or of *electron affinities* of the radicals resulting from deelectronation thereof. We use the term *deelectronation energy* to emphasize that it is a property of the anion, to free the name of the quantity from notation of the method used to determine it, and because the term *ionization energy of an anion* would be inappropriate for a process which accomplishes the opposite of ionization.

(47) Smyth, K. C.; Brauman, J. I. *J. Chem. Phys.* **1972**, 56, 1132. Reed, K. J.; Brauman, J. I. *Ibid.* **1974**, *61*, 4830. Richardson, J. H.; Stephenson, L. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1975**, *97*, 2967. Zimmerman, A. H.; Brauman, J. I. *Ibid.* **1977**, *99*, 3565. Zimmerman, A. H.; Reed, K. J.; Brauman, J. I. *Ibid.* **1977**, *99*, 7203. Janousek, B. K.; Zimmerman, A. H.; Reed, K. J.; Brauman, J. I. *Ibid.* **1978**, *100*, 6142.

determinations have been corroborated by McMahon and Kebarle[48] by means of a different experimental method. Inasmuch as one might expect a low deelectronation energy to correlate with high nucleophilicity,[49] we list in order of increasing deelectronation energy (shown in parentheses) a number of nucleophiles of interest in the present context, as follows: NH_2^- (0.74 eV), PH_2^- (1.25 eV), $NCCH_2^-$ (1.51 eV), acetone enolate ion (1.78 eV), pinacolone enolate ion (1.86 eV), t-BuO$^-$ (1.87 or 1.90 eV), PhO$^-$ (2.36 eV), and PhS$^-$ (2.47 eV).[47] Taking PH_2^- as representative of Ph_2P^-, we do indeed see some nucleophiles rather reactive toward phenyl radical at the start of this list, and the relatively unreactive PhS$^-$ at the end. However, the unreactive t-BuO$^-$ has nearly the same deelectronation energy as the reactive pinacolone enolate ion, and the unreactive PhO$^-$ is lower than the significantly reactive PhS$^-$. Without doubt, solvation considerably affects deelectronation energies. Nevertheless, it does not seem possible to ascribe differences in nucleophilic reactivity toward the phenyl radical solely to differences in deelectronation energy.

Deviant Behavior in Some Experiments with Diphenylphosphide Ion. Whereas consistent relative reactivity is displayed by Ph_2P^- in dark reactions with iodobenzene (experiment 16) or *p*-iodotoluene (experiments 17, 26, and 27) and in photostimulated reactions with *p*-bromo- and *p*-iodotoluene (experiments 18 and 20), extraordinarily high relative reactivity for Ph_2P^- is indicated in a dark reaction with *p*-bromotoluene (experiment 19) in in photostimulated reactions with chloro- and bromobenzene (experiments 21 and 28). Why the deviant results in these last three experiments? Is a competing mechanism involved, or can the result be interpreted within the framework of the usual $S_{RN}1$ hypothesis?

One conceivable competing mechanism is the familiar S_NAr, which proceeds via a σ-adduct intermediate. For it, the usual order of halogen mobility is: $F >> Cl \sim Br > I$.[15,16] However, our data (including an attempted competitive reaction between Ph_2P^- and pinacolone enolate ion with *p*-fluorotoluene, photostimulated with 16 lamps, not tabulated because no detectable products were formed in 6.5 h) express the usual $S_{RN}1$ mobility order: $I > Br > Cl > F$.[14] A second conceivable competing mechanism would proceed via aryne intermediates. It is disqualified for present purposes by the fact that in experiments with *p*-halotoluenes, including especially one in which Ph_2P^- seems to show deviant behavior (experiment 19), the substitution products formed were strictly of para orientation.

It should be noted that consistent relative reactivity is demonstrated for aryl iodides both in the dark and under illumination, and for *p*-bromotoluene under illumination, suggesting that the same propagation cycle obtains irrespective of the method of initiation, and that the halogen is gone at the point of interaction with the nucleophile. Second, the incidence of deviant behavior is capricious; experiment 20 (with *p*-bromotoluene and illumination) seems well behaved while experiment 28 (with PhBr and illumination) deviates. Also, the deviation in experiment 19 or 28 is much greater than that in experiment 21 (with PhCl and illumination). Again, the relative reactivity for Ph_2P^- implied by experiment 28 is considerably less than that implied by experiment 19. The data suggest that some adventitious factor affects some experiments more seriously than others.

It is noteworthy that most of the deviant reactions are of longer duration, say, 600 s or longer, while most of the well-behaved ones are of shorter duration. Possibly the slow entry of dioxygen into the system, as a trace contaminant in the dinitrogen used or otherwise, may have caused some interference, maybe by forming the potentially troublesome $Ph_2P{-}PPh_2$, maybe in some other way. Further study of this question is planned.

Experimental Section

General Procedure for Competition Experiments. All experiments were conducted under a positive pressure of dry dinitrogen in Pyrex glassware that had been flamed in a stream of dry ninitrogen. Ammonia (50 to 150 mL) was distilled from sodium into a three-neck flask flushed with N_2 and equipped with a cold-finger type condenser (with 2-propanol and solid CO_2 in the coolant well) and a serum cap. Under magnetic stirring, weighed amounts of freshly resublimed potassium *tert*-butoxide (t-BuOK), biphenyl (internal standard), and solid substrates or nucleophile conjugate acids were added through paper funnels. Liquid substrates or nucleophile conjugate acids were added from a syringe weighed before and after injection. The resulting reactant concentrations as given in Table I are somewhat approximate owing to the difficulty of measuring the ammonia volume accurately with the procedure employed. In all cases the amount of t-BuOK used was in excess of that required to deprotonate the two nucleophile conjugate acids;[50] representative concentrations of free t-BuOK in reaction solutions were 0.057 M in experiment 1, 0.056 M in experiment 13, and 0.0052 M in experiment 20. After all reactants except the substrate had been added, the exterior surface of the flask was washed with acetone to remove frost, the flask with condenser and dinitrogen connection was mounted in a Rayonet RPR-100 photochemical reactor, the substrate was quickly added, and the flask was either maintained in the dark or subjected to irradiation as stated in Table I. Normally the reactor was equipped with 16 lamps emitting maximally at 350 nm but in some cases, as stated in footnotes to Table I, only one lamp was used or 16 lamps emitting maximally at 300 nm were used. At times stated in Table I, irradiation was briefly interrupted and samples of ca. 3 mL were removed by means of little glass ladles and immediately quenched by pouring them into 1.5 mL of a 2 M solution of ammonium nitrate in water. Each quenched sample was extracted with diethyl ether, the ether solution was concentrated to a small volume, and the concentrate was analyzed by GLC. Samples taken by ladle at the end of irradiation were found to give essentially the same product analysis as did the whole remaining pot contents when similarly quenched and analyzed. GLC analysis was performed on a Hewlett-Packard 5750 flame ionization instrument. A column, 183 cm × 3.2 mm, of 10% silicon rubber (UC-W98) on 80–100 mesh Chromosorb WAW DMCS was employed. Molar response factors were determined and used in the calculation of GLC results in all cases.

When one of the competing nucleophiles was $Ph_2P^-K^+$, the product analysis was conducted a little differently. The ether extracts after quenching were divided into two parts; one part was analyzed directly by GLC to determine the product from the competing nucleophile; the other part was washed twice with 5% aqueous H_2O_2 solution, and then with 10% aqueous NaOH, and subjected to GLC analysis. The latter treatment oxidized Ph_3P to Ph_3PO, or p-$CH_3C_6H_4PPh_2$ to p-$CH_3C_6H_4POPh_2$; these phosphine oxides are stable and easily determined by GLC analysis.

The concentration of biphenyl internal standard was typically about 0.01 M. On one experiment in which PhBr reacted with a mixture of $(EtO)_2PO^-K^+$ and potassium pinacolone enolate, at concentration levels similar to experiment 6 except that biphenyl was omitted, the reactivity ratio was essentially the same as when biphenyl was present. In this experiment, no biphenyl was detectable as a reaction product.

After experiments 14, 15, and 24 had been completed, it was discovered that the Ph_2PHO used to prepare the Ph_2PO^- reagent was contaminated by 0.9% of Ph_3PO. The yields of Ph_3PO obtained in these experiments were appropriately corrected. Experiment 25 utilized the same reagents as experiment 24 but because *p*-iodotoluene was the substrate there was no need to apply such a correction; it is reassuring that the reactivity ratios from experiments 24 and 25 are nearly the same.

Calculation of Relative Reactivities. Equation 6 was employed, where $[Y^-]_0$ and $[Z^-]_0$ are initial concentrations and $[ArY]_t$ and $[ArZ]_t$ are concentrations of products at time t.[13] This equation is based on an assumption that both Y^- and Z^- reactions with the reactive intermediate are first order in nucleophile.

$$\frac{k_{Y^-}}{k_{Z^-}} = \frac{\ln [Y^-]_0/([Y^-]_0 - [ArY]_t)}{\ln [Z^-]_0/([Z^-]_0 - [ArZ]_t)} \tag{6}$$

Reaction of Diethyl Phenylphosphonate with Pinacolone Enolate Ion. In experiment 10, Table I, the major change in apparent relative reactivity with the passage of time suggested that the phosphonate ester

---

(48) McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1974**, *96*, 5940; **1977**, *99*, 2222.

(49) Bunnett, J. F. *Annu. Rev. Phys. Chem.* **1963**, *14*, 271.

(50) We do not know the pK_a of t-BuOH or of pinacolone in ammonia. In Me_2SO, the pK_a of t-BuOH is 32.2[51] and that of acetone is 26.5.[52] Inasmuch as NH_3 resembles Me_2SO in pK_a (34.6[53] vs. 35.1[51]), it is probable that the relative pK_a's of t-BuOH and acetone are similar in the two solvents. It is also probable that the pK_a's of acetone and pinacolone are nearly the same. These considerations as well as practical experience in our laboratory indicate that a small excess of t-BuOK is sufficient to convert pinacolone fully to its enolate ion.

(51) Olmstead, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3295.

(52) Bordwell, F. G., *Faraday Symp. Chem. Soc.* **1975**, *10*, 100.

(53) Lagowski, J. J. *J. Chem. Educ.* **1978**, *55*, 752.

product was slowly consumed by reaction with the enolate ion nucleophile. A mixture of $PhPO(OEt)_2$ (0.023 M), biphenyl (0.011 M), and potassium pinacolone enolate (0.101 M) in 90 mL of ammonia was prepared and treated much as in our general procedure for competition experiments. Samples taken at various times showed the following percentages of the original $PhPO(OEt)_2$ to remain as such: 900 s, 99.7%; 1800 s, 79.6%; 3600 s, 65.0%; 8100 s, 26.1%. A byproduct of this experiment was a small amount of 2,2,7,7-tetramethyloctan-3,6-dione, recognized by its ^1H NMR spectrum matching that published by Komin and Wolfe,[26] as well as by its mass spectrum fragmentation pattern.

Aluminum-27 Nuclear Magnetic Resonance Study of the Room-Temperature Melt $AlCl_3$/*n*-Butylpyridinium Chloride

Joel L. Gray and Gary E. Maciel*

Contribution from the Department of Chemistry,
Colorado State University, Fort Collins, Colorado 80523. Received November 17, 1980

Abstract: ^{27}Al NMR spectra were obtained on liquid samples consisting nominally of mixtures of $AlCl_3$ and *n*-butylpyridium chloride at various mole ratios and at various temps. Previous suggestions of the structure of the components of these melts have been supported, and the ^{27}Al NMR parameters of the $AlCl_4^-$ and $Al_2Cl_7^-$ ions in these melts have been determined. A chemical exchange rate has been estimated by spectral simulation. The species present in a solution obtained by adding $(CH_3)_4NI$ to a 1.4-to-1 melt ($AlCl_3$-to-BuPyCl) have been identified by ^{27}Al NMR.

Studies of molten salt systems involving mixtures of aluminum chloride and halide salts have been reported. For example, Boxall et al.[1] have investigated the important equilibria occurring in fused $NaCl/AlCl_3$ mixtures by electrochemical techniques. In the temperature range from 175 to 300 °C $NaCl/AlCl_3$ mixtures melt, and reaction 1 occurs essentially quantitatively. This system can be described by (1) and equilibria 2–5.[1] At 175 °C the following values of the equilibrium constants were determined by Osteryoung and co-workers: $K_3 = 2.86 \times 10^7$, $K_4 = 2.4 \times 10^4$, and $K_5 = 1.06 \times 10^{-7}$.

$$Cl^- + AlCl_3 \xrightleftharpoons{K_2} AlCl_4^- \tag{1}$$

$$Cl^- + Al_2Cl_3 \xrightleftharpoons{K_1} AlCl_4^- + AlCl_3 \tag{2}$$

$$2AlCl_3 \xrightleftharpoons{K_3} Al_2Cl_6 \tag{3}$$

$$AlCl_3 + AlCl_4^- \xrightleftharpoons{K_4} Al_2Cl_7^- \tag{4}$$

$$2AlCl_4^- \xrightleftharpoons{K_5} Al_2Cl_7^- + Cl^- \tag{5}$$

Osteryoung and co-workers have studied molten salt systems involving 1-*n*-butylpyridium chloride/$AlCl_3$ (BPC/$AlCl_3$) and 1-*n*-butylpyridium bromide/$AlCl_3$ by Raman spectroscopy,[2] by electrochemical methods,[3] and by ^1H and ^{13}C NMR.[4] For the BPC/$AlCl_3$ case Gale and Osteryoung[3] found that the equilibrium constant for (5) is less than 3.83×10^{-13} at 30 °C. Gale, Gilbert, and Osteryoung[2] concluded that $AlCl_4^-$ species have T_d symmetry and that $Al_2Cl_7^-$ species possibly have D_{3d} symmetry. However, X-ray diffraction studies of $Al_2Cl_7^-$ in a solid-state system indicate a nonlinear Al–Cl–Al bridge and the arrangement of Cl atoms about each Al atom approaching tetrahedral symmetry (the Al–Cl bond length in the bridge is only about 7% longer than the terminal Al–Cl bond length).[5]

To our knowledge no ^{27}Al NMR data have been reported on the "room-temperature" molten salt system BPC/$AlCl_3$. Anders and Plambeck[6] have reported ^{27}Al NMR data on the molten $NaCl/KCl/AlCl_3$ system at 170 °C. ^{27}Al NMR studies on the BPC/$AlCl_3$ system provide one the important opportunity of studying the anionic chemistry of $AlCl_4^-$ and $Al_2Cl_7^-$ in the molten state at lower temperature (near room temperature), where chemical exchange rates are expected to be lower than in the high-temperature melt.

Experimental Section

Materials. 1-*n*-Butylpyridium chloride was prepared by the method outlined by Gale, Gilber, and Osteryoung.[2] The purified crystals had a melting point of 131–133 °C (lit.[2] 131.5 °C). $AlCl_3$ (Fluka) was reagent grade purity and was used without further purification. Tetramethylammonium iodide (Eastman) was also reagent grade and was dried under high vacuum at ambient temperature.

All materials were stored under an anhydrous nitrogen gas atmosphere in a dry box. All molten salt preparations and manipulations were performed in the dry box. Melts were generated by adding a weighed amount of $AlCl_3$ to a weighed amount of 1-*n*-butylpyridium chloride. Immediately following the addition, the mixtures become hot and fumes appeared, which created an uncertainty in the final melt composition. To minimize this uncertainty, we tightly capped the mixtures as soon as possible after the $AlCl_3$ addition.

NMR Measurements. Most aluminum-27 spectra were recorded on a Bruker HFX-90 spectrometer described elsewhere.[7] The receiver coil was tuned to optimize the detection of aluminum-27 resonances at 23.44 MHz. No provision was made to reference the observed aluminum-27 resonance frequencies, except by sample substitution. Unless otherwise stated, the NMR measurements were made at 36 °C. The spectra in Figure 2 were recorded on a Nicolet NT-150 spectrometer.

Viscosity Measurements. Measurements were made by using a Kimax 300 Ostwald viscometer in a constant temperature bath of 41.0 ± 0.1 °C. The interior of the viscometer and its contents were maintained under anhydrous nitrogen gas atmosphere. Plumb lines were used to maintain a vertical alignment of the viscometer. A calibration standard was prepared by using glycerol (Baker) and distilled H_2O. This mixture had a specific gravity of 1.203 (78.0% w/w glycerol) at 20 °C and a viscosity of 17.1 cP at 41.0 ± 0.1 °C.

---

[1] Boxall, L. G.; Jones, H. L.; Osteryoung, R. A. *J. Electrochem. Soc.* **1973**, *120*, 223–231.

[2] Gale, R. J.; Gilbert, B.; Osteryoung, R. A. *Inorg. Chem.* **1978**, *17*, 2728–2729.

[3] (a) Gale, R. J.; Osteryoung, R. A. *Inorg. Chem.* **1979**, *18*, 1603–1605. (b) Gale, R. J.; Gilbert, B.; Osteryoung, R. A. *Inorg. Chem.* **1979**, *18*, 2723–2725.

[4] Robinson, J.; Bugle, R. C.; Chum, H. L.; Koran, D.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 3776–3779.

[5] Couch, T. W.; Lokken, D. A.; Corbett, J. D. *Inorg. Chem.* **1972**, *11*, 357–362.

[6] Anders, U.; Plambeck, J. A. *J. Inorg. Nucl. Chem.* **1978**, *40*, 387–388.

[7] Ackerman, J. J. H.; Maciel, G. E. *J. Magn. Reson.* **1976**, *23*, 67–69.

[8] Kidd, R. G.; Traux, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 6867–6869.

0002-7863/81/1503-7147$01.25/0