

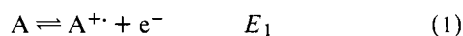
Reactions of Cation Radicals of EE Systems. 7. Mechanistic Considerations and Relative Reactivities of Nucleophiles in Reaction with the Cation Radical of 9,10-Diphenylanthracene¹

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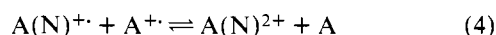
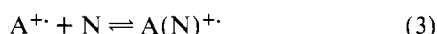
Abstract: The reactions of the cation radical of 9,10-diphenylanthracene (DPA⁺) with neutral protic, neutral aprotic, and anionic aprotic nucleophiles in acetonitrile have been examined by spectroelectrochemical and stopped-flow kinetic methods. In these reactions, both reduction of and addition to the cation radical are observed. It is found that reaction type (electron transfer vs. addition) can be predicted from a consideration of the oxidation potential of the nucleophile relative to that of DPA. For those cases in which the nucleophile behaves as a reductant (H₂S, Br⁻, I⁻, SCN⁻, and CN⁻), the experimental rate law is found to be first order with respect to both nucleophile and cation radical concentrations and independent of the concentration of the precursor (DPA), indicating rate-determining encounter between nucleophile and cation radical. Furthermore, the dynamics of the addition reactions of H₂O, 4-cyanopyridine, pyridine, and piperidine to DPA⁺ are described by a rate law of the same form. In concert with the observed reaction stoichiometries, these kinetic data indicate that addition occurs via the half-regeneration mechanism. The relative reactivities of these nucleophiles toward DPA⁺ in acetonitrile (both addition and electron transfer cases) are found to parallel those reported for these same nucleophiles in the S_N2 displacements of iodide from methyl iodide in methanol. In addition to affording a means of predictability of the dynamics of reactions of nucleophiles with this carbon-centered cation radical, the linearity of this correlation which includes both electron transfer and addition reactions suggests a common transition state for both reaction types.

The elucidation of the mechanisms by which hydrocarbon and heterocyclic fused-ring cation radicals react with "electron-rich" species (nucleophiles and reducing agents) continues to be an active area of research.³⁻⁷ Of particular interest are those systems in which the substrate, A, may be categorized as an "EE" system. That is, within the potential region availed by the solvent of choice, the EE substrate undergoes two successive, independent, monoelectronic oxidation steps.



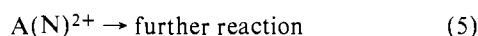
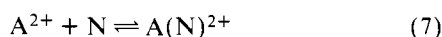
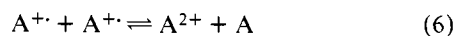
The first of these (eq 1) leads to the formation of the cation radical, A⁺, from the substrate, and the second (eq 2), which requires a more anodic formal potential ($E_2 > E_1$), affords the dication by oxidation of the cation radical. In delineating the mechanism of addition of a nucleophile, N, to this type of cationic system, one must consider the multiplicity of pathways by which consumption of the cation radical may proceed. In most general terms, one strives to establish whether the cation radical is consumed via direct reaction with nucleophile (half-regeneration^{8,9} or complexation^{10,11} mechanism, Scheme I)

Scheme I



or via indirect reaction involving the dication, which arises from the disproportionation of the cation radical (eq 6), as the species undergoing reaction with the nucleophile (disproportionation mechanism,^{12,13} Scheme II).

Scheme II



From thermodynamic considerations, the latter scheme *must be addressed*, since a solution of cation radical must indeed contain a finite concentration of the more reactive dication. It is perhaps most accurate to say that one attempts to discern, if possible, which of these two competing pathways predominates in a given cation radical/nucleophile reaction, since both are likely to proceed to a certain extent in all cases. The importance of the relative rates of all of the elementary steps of each mechanism, in concert with the free-energy changes associated with the reversible processes, will dictate which of these pathways predominates. The details of such evaluations have been treated in depth by several authors,^{1,10,11,14,17} and need not be repeated here.

In these laboratories, several EE cation radical/nucleophile systems have been studied in detail,^{1,14-17} each having been shown to proceed primarily by the half-regeneration mechanism. The experimental rate laws determined for many of these systems have been found to be quite complex. Notable exceptions are those involving the reactions of the carbon-centered 9,10-diphenylanthracene (DPA) cation radical (DPA⁺) where, in all cases save one (the reaction of DPA⁺ with chloride¹⁷), a rate law which is first order in both cation radical and nucleophile, and independent of precursor concentration, has been found to appropriately describe the dynamics observed for these reactions.

Consequently, the question of the general applicability of the half-regeneration mechanism as an adequate description of the reactions of a wide variety of nucleophiles with DPA⁺ will be addressed and furthermore, where possible, a scale of relative reactivities of these nucleophiles toward this kinetically "well-behaved" cation radical will be defined. To this end, representative nucleophiles from three classes (neutral aprotic, neutral protic, and anionic aprotic) have been studied in reaction with DPA⁺. For certain of the nucleophiles selected, addition to DPA⁺ is observed, while for others electron transfer (reduction of DPA⁺) is noted. This then provides another dimension to the present study: that of a comparison of "nucleophilic reactivity"¹⁸ in the context of these two apparently divergent reaction types. Under the reaction conditions employed in this work, kinetic parameters have been

Table I. Stoichiometries and Products Observed for the Reactions of DPA⁺ with Various Nucleophiles^a

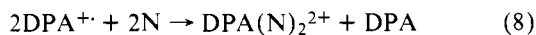
Nucleophile	% DPA regenerated ^b	Observed products ^c	Ref
H ₂ O	51 (±1) ^d	DPA(OH) ₂	9, 20, 21
H ₂ S	97 (±3)	S ₁ , S ₂ , . . . , S ₈	9, 16
py	50 (±2)	DPA(py) ₂ ²⁺	22
CNpy	51 (±4)	<i>e</i>	21
Et ₃ N	50 (±3)	DPA(Et ₃ N) ₂ ²⁺	22
Pip	54 (±5)	<i>e</i>	21
Cl ⁻	53 (±3)	DPA(Cl) ₂	9, 17
Br ⁻	95 (±4)	Br ₂	9, 21
I ⁻	98 (±3)	I ₃ ⁻	9, 21
CN ⁻	97 (±5)	<i>f</i>	21, 23
SCN ⁻	98 (±3)	(SCN) _x	9, 21

^a DPA⁺ electrogenerated from DPA at a Pt anode in CH₃CN containing 0.10 M TBAP. ^b As % DPA regenerated from DPA⁺ originally present. DPA monitored spectrophotometrically, after the manner of Sioda.⁹ ^c Other than DPA; DPA(OH)₂ = 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene; DPA(py)₂²⁺ = 9,10-diphenyl-9,10-dipyridinium-9,10-dihydroanthracene (as perchlorate); DPA(Et₃N)₂²⁺ = 9,10-diphenyl-9,10-di(triethylammonium)-9,10-dihydroanthracene (as perchlorate); DPA(Cl)₂ = 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene; (SCN)_x = parathiocyanogen. ^d Parentheses contain one standard deviation. ^e Reaction products other than DPA not isolated or characterized. For CNpy, the anticipated addition product is 9,10-di(*p*-cyanopyridinium)-9,10-diphenyl-9,10-dihydroanthracene dication by analogy to DPA(py)₂²⁺. For Pip reaction, anticipated addition product is 9,10-diphenyl-9,10-dipiperidiny-9,10-dihydroanthracene by analogy to DPA(OH)₂. ^f The fate of CN⁻ resulting from direct electron transfer from CN⁻ to DPA⁺ is unknown. This intermediate has been suggested to dimerize²³ or undergo reaction with the solvent, acetonitrile.²⁴

determined which allow the calculation of a "nucleophilicity" parameter analogous to that defined by Swain and Scott.¹⁹ These parameters are valid for both addition and electron transfer reactions and are compared with those reported for other reaction types. The resulting correlation is discussed in terms of the two reaction modes for DPA⁺.

Results and Discussion

Stoichiometry. The nucleophiles selected for this study include H₂O, H₂S, pyridine (py), 4-cyanopyridine (CNpy), piperidine (Pip), triethylamine (Et₃N), Cl⁻, Br⁻, I⁻, CN⁻, and SCN⁻. The stoichiometries of the reactions of these nucleophiles with DPA⁺ and the products isolated and characterized therefrom are summarized in Table I. As can be seen from these data, two reaction types are in evidence. The first involves the addition of nucleophile to DPA⁺ to yield equimolar amounts of 9,10-disubstituted 9,10-diphenyl-9,10-dihydroanthracene (DPA(N)₂²⁺) and the DPA precursor:²⁵



The second reaction type involves complete regeneration of DPA, i.e., reduction of DPA⁺ by the nucleophile. For the halides and pseudohalides, X⁻, where electron transfer products are observed, the equation



appropriately describes the general stoichiometric relationship. In the case of SCN⁻, higher degrees of aggregation of the oxidized form of the nucleophile are found (Table I), while for I⁻, the corresponding perhalide ion is formed in the presence of excess iodide,²⁶ according to the equation



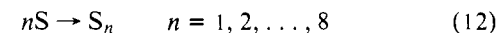
The formation of perbromide in the acetonitrile medium em-

Table II. Comparison of DPA⁺/Nucleophile Reaction Type with Relative Redox Potentials of Nucleophiles and DPA

Species	E _{1/2} , V ^a	Ref	Reaction type ^b
H ₂ S	0.14	27	ET
I ⁻	0.50	28	ET
CN ⁻	<0.60	24	ET
SCN ⁻	0.69	28	ET
Br ⁻	0.85	28	ET
Cl ⁻	1.11	28	A
DPA	1.28	22	-
H ₂ O	1.6	29	A
Et ₃ N	1.7	29	A
Pip	1.7	29	A
py	2.3	29	A
CNpy	>2.5	21	A

^a Voltammetric half-wave potentials for oxidation at a platinum anode in CH₃CN vs. aqueous saturated calomel reference electrode. ^b ET = electron transfer (eq 9, 11); A = addition (eq 8).

ployed here is apparently not thermodynamically favored even with large excess of bromide.²⁶ The case of H₂S is unique among the reactions studied in the sense that this species functions as a formal two-electron reducing agent:



A perusal of the half-wave potentials of these nucleophiles relative to that of DPA (Table II) indicates that a good measure of predictability of reaction type resides in this parameter. As pointed out by Ebersson,²⁹ the literature detailing the types of reactions undergone by several nucleophiles with the cation radicals of perylene, thianthrene, phenothiazine, and dibenzodioxin affords no discernible reactivity pattern based on the oxidation potential of the nucleophile (a possible exception is the perylene cation radical system). Clearly, the data given in Table II indicate that DPA⁺ is a definite exception. As we shall see, this may be a manifestation of the kinetic simplicity of the DPA⁺ reactions compared to the complex kinetic behavior typical of the thianthrene^{10,11,14} and 10-phenylphenothiazine¹ cation radicals in which the relative stability of intermediates may alter the predictability of reaction type. Unfortunately, the limited kinetic and mechanistic information available for the reactions of other cation radicals does not allow for a complete discussion and evaluation of such a hypothesis.

Kinetics. A reexamination of Schemes I and II shows that identical stoichiometries are predicted for nucleophilic addition via both the half-regeneration mechanism and the disproportionation route, and consequently a detailed kinetic analysis is required prior to assignment of the predominant pathway followed in these reactions. The kinetic parameters for addition reactions of DPA⁺, as well as those for cases where electron transfer prevails, are given in Table III. In all cases but the Cl⁻ and Et₃N reactions,³¹ the experimental rate law describing the observed dynamics for the disappearance of DPA⁺ assumes the form

$$d[\text{DPA}^+]/dt = -k_{\text{obsd}}[\text{DPA}^+][\text{N}] \quad (13)$$

When Cl⁻ or Et₃N are reacted with DPA⁺, the rate of reaction is found to depend upon DPA⁺ concentration in a second-order fashion:

$$d[\text{DPA}^+]/dt = -k_{\text{obsd}}[\text{DPA}^+]^2[\text{N}] \quad (14)$$

The consequences of these results are manifold. Firstly, for the addition reactions, the lack of any discernible effect of DPA concentration on the observed kinetics clearly implicates the half-regeneration mechanism (Scheme I) as the predominant

Table III. Kinetic Parameters Determined for the Reaction of Electrogenerated DPA^{•+} with Various Nucleophiles in Acetonitrile at 25 °C^a

Nucleophile, N	Technique ^b	[DPA ^{•+}] ₀ , M	Order in [DPA ^{•+}]	[N] ₀ , M	Order in [N]	Replicates	k _{obsd.} ^{c,d} M ⁻¹ s ⁻¹	Ref
H ₂ O	SE	5.0 × 10 ⁻⁴	1	2.50	1	6	1.27 (±0.08) × 10 ⁻¹	30, f
H ₂ O	SE	5.0 × 10 ⁻⁴	1	3.00	1	6	1.26 (±0.06) × 10 ⁻¹	30, f
H ₂ O	SE	5.0 × 10 ⁻⁴	1	4.00	1	4	1.19 (±0.10) × 10 ⁻¹	30, f
H ₂ O	SF	5.0 × 10 ⁻⁵	1	5.1 × 10 ⁻³	1	3	1.23 (±0.08) × 10 ⁻¹	17
H ₂ O	SF	5.0 × 10 ⁻⁵	1	1.50	1	12	1.33 (±0.02) × 10 ⁻¹	17
H ₂ O (av)			1		1	31	1.28 (±0.06) × 10 ⁻¹	e
H ₂ S	SE	1.0 × 10 ⁻³	1	1.55 × 10 ⁻²	1	4	8.2 (±1.4)	16, f
H ₂ S	SE	1.0 × 10 ⁻³	1	2.95 × 10 ⁻²	1	19	1.22 (±0.17) × 10 ¹	16, f
H ₂ S	SE	1.0 × 10 ⁻³	1	7.02 × 10 ⁻²	1	12	1.34 (±0.12) × 10 ¹	16, f
H ₂ S	SE	1.0 × 10 ⁻³	1	1.06 × 10 ⁻¹	1	16	1.32 (±0.06) × 10 ¹	16, f
H ₂ S	SF	5.0 × 10 ⁻⁵	1	2.73 × 10 ⁻²	1	14	1.12 (±0.20) × 10 ¹	16, f
H ₂ S	SF	5.0 × 10 ⁻⁵	1	6.96 × 10 ⁻²	1	23	1.63 (±0.12) × 10 ¹	16, f
H ₂ S	SF	5.0 × 10 ⁻⁵	1	8.25 × 10 ⁻²	1	23	1.48 (±0.06) × 10 ¹	16, f
H ₂ S	SF	5.0 × 10 ⁻⁵	1	8.80 × 10 ⁻²	1	15	1.28 (±0.05) × 10 ¹	16, f
H ₂ S	SF	5.0 × 10 ⁻⁵	1	1.40 × 10 ⁻¹	1	17	1.12 (±0.14) × 10 ¹	16, f
H ₂ S (av)			1		1	143	1.32 (±0.24) × 10 ¹	e, f
CNpy	SE	1.0 × 10 ⁻³	1	1.0 × 10 ⁻¹	1	6	1.41 (±0.09) × 10 ²	21, e, h
py	SE	1.0 × 10 ⁻³	1	5.14 × 10 ⁻⁵	1	6	3.38 (±0.74) × 10 ⁴	15, f
py	SE	1.0 × 10 ⁻³	1	1.05 × 10 ⁻⁴	1	8	3.58 (±0.88) × 10 ⁴	15, f
py	SE	1.0 × 10 ⁻³	1	2.07 × 10 ⁻⁴	1	8	3.56 (±0.66) × 10 ⁴	15, f
py	SE	1.0 × 10 ⁻³	1	4.84 × 10 ⁻⁴	1	8	4.26 (±0.84) × 10 ⁴	15, f
py	SE	1.0 × 10 ⁻³	1	1.02 × 10 ⁻³	1	7	3.68 (±0.54) × 10 ⁴	15, f
py	SE	1.0 × 10 ⁻³	1	1.02 × 10 ⁻³	1	6	3.84 (±0.42) × 10 ⁴	21
py (av)			1		1	43	3.72 (±0.76) × 10 ⁴	e
Br ⁻	SF	2.9 × 10 ⁻⁵	1	4.25 × 10 ⁻⁵	1	5	6.14 (±0.53) × 10 ⁵	21
Br ⁻	SF	3.3 × 10 ⁻⁵	1	2.66 × 10 ⁻⁴	1	5	8.04 (±0.28) × 10 ⁵	21
Br ⁻	SF	4.5 × 10 ⁻⁵	1	5.31 × 10 ⁻⁴	1	9	6.70 (±0.47) × 10 ⁵	21
Br ⁻ (av)			1		1	19	6.91 (±0.85) × 10 ⁵	e
SCN ⁻	SF	6.2 × 10 ⁻⁶	1	3.18 × 10 ⁻⁵	1	5	3.10 (±0.05) × 10 ⁶	21
SCN ⁻	SF	1.0 × 10 ⁻⁵	1	6.35 × 10 ⁻⁵	1	8	3.36 (±0.15) × 10 ⁶	21
SCN ⁻	SF	1.1 × 10 ⁻⁵	1	1.27 × 10 ⁻⁴	1	5	3.57 (±0.23) × 10 ⁶	21
SCN ⁻ (av)			1		1	18	3.35 (±0.23) × 10 ⁶	e
CN ⁻	SF	9.6 × 10 ⁻⁶	1	2.23 × 10 ⁻⁵	1	5	7.50 (±0.56) × 10 ⁶	21
CN ⁻	SF	8.8 × 10 ⁻⁶	1	4.47 × 10 ⁻⁵	1	7	6.59 (±0.79) × 10 ⁶	21
CN ⁻	SF	6.6 × 10 ⁻⁶	1	8.94 × 10 ⁻⁵	1	7	5.19 (±0.84) × 10 ⁶	21
CN ⁻ (av)			1		1	19	6.30 (±1.20) × 10 ⁶	e
I ⁻	SF	5.5 × 10 ⁻⁶	1	1.22 × 10 ⁻⁵	1	5	1.42 (±0.47) × 10 ⁷	21
I ⁻	SF	1.6 × 10 ⁻⁵	1	2.45 × 10 ⁻⁵	1	9	1.81 (±0.55) × 10 ⁷	21
I ⁻	SF	2.3 × 10 ⁻⁵	1	4.89 × 10 ⁻⁵	1	6	1.09 (±0.31) × 10 ⁷	21
I ⁻ (av)			1		1	20	1.49 (±0.55) × 10 ⁷	e
Pip	SF	2.4 × 10 ⁻⁵	1	5.51 × 10 ⁻⁵	1	5	2.54 (±0.36) × 10 ⁷	21, e
Cl ⁻	SF	1.0 × 10 ⁻⁵	2	4.73 × 10 ⁻⁵	1	5	8.36 (±0.14) × 10 ⁹	17, g
Cl ⁻	SF	2.5 × 10 ⁻⁵	2	4.73 × 10 ⁻⁴	1	15	9.48 (±0.36) × 10 ⁹	17, g
Cl ⁻	SF	2.7 × 10 ⁻⁵	2	4.73 × 10 ⁻³	1	5	9.50 (±0.26) × 10 ⁹	17, g
Cl ⁻ (av)			2		1	25	9.26 (±0.62) × 10 ⁹	e, g
Et ₃ N	SF	3.2 × 10 ⁻⁵	2	5.88 × 10 ⁻⁵	1	5	8.0 (±2.8) × 10 ¹³	21, e, g

^a Kinetics monitored for at least 2 half-lives; TBAP present at 0.10 M in all cases except as noted. In all cases, variation of [DPA] gave rise to no variation in k_{obsd.} ^b SE = spectroelectrochemistry; SF = stopped-flow kinetic spectrophotometry. ^c According to eq 13. Coefficients of correlation for kinetic fits were typically 0.995 and >0.985 in all cases. ^d Parentheses contain one standard deviation in observed rate constant. ^e Weighted average value of k_{obsd.} ^f Tetraethylammonium perchlorate present at 0.10 M. ^g Termolecular rate constants according to eq 14 (M⁻² s⁻¹). ^h CNpy reaction order assigned by analogy to py.

pathway by which nucleophilic attack proceeds. Disproportionation (Scheme II) must be considered to account for only a very small fraction of the overall consumption of DPA^{•+}. The general applicability of the half-regeneration mechanism to the addition of nucleophiles to DPA^{•+} is indicated, although the rate-determining step may reside in either the attack of nucleophile on the cation radical (eq 3, forward step) or in the electron transfer between reversibly formed cation radical/nucleophile adduct, A(N)^{•+}, and free cation radical (eq 4, forward step). The further ramifications of these assignments are the *apparent* irreversibility of the adduction step (eq 3) in the former case and the *apparent* irreversibility of the electron transfer process (eq 4) in the latter case, presumably attributable to the high velocity of the subsequent steps which rapidly

consume the products of the respective rate-determining steps.

Secondly, with the exception of the Cl⁻ and Et₃N reactions, elementary bimolecular rate constants, *k*, for *both electron transfer and addition reactions* are at hand, allowing for a direct comparison of the kinetic parameters of these different reaction types. Stoichiometric considerations (eq 8, 9, and 11) dictate that the bimolecular rate constants for the addition reactions (H₂O, py, CNpy, and Pip) and for the electron transfer reaction of H₂S and DPA^{•+} are given by

$$k = k_{\text{obsd}}/2 \quad (15)$$

while for the monoelectronic reducing agents (Br⁻, I⁻, SCN⁻, and CN⁻), it is given by

Table IV. Nucleophilicity Parameters for Reactions of Various Nucleophiles, N, with DPA⁺ in Acetonitrile and with Methyl Iodide in Methanol^a

Nucleophile, N	$k_N, {}^{b,c} \text{M}^{-1} \text{s}^{-1}$	$n_{\text{DPA}^+, \text{CH}_3\text{CN}}^{\text{N}/\text{H}_2\text{O}}$	$n_{\text{CH}_3\text{I}, \text{CH}_3\text{OH}}^{\text{N}/\text{CH}_3\text{OH}}$	Ref ^d
H ₂ O	$6.45 (\pm 0.28) \times 10^{-2}$	0.00	1.35	33
H ₂ S	$6.6 (\pm 1.2)$	2.01	3.34	34
CNpy	$7.03 (\pm 0.47) \times 10$	3.04	3.76	35
py	$1.86 (\pm 0.38) \times 10^4$	5.46	5.23	36
Br ⁻	$6.91 (\pm 0.85) \times 10^5$	7.03	5.79	36
SCN ⁻	$3.35 (\pm 0.23) \times 10^6$	7.72	6.70	36
CN ⁻	$6.3 (\pm 1.2) \times 10^6$	7.99	6.70	36
Pip	$1.26 (\pm 0.18) \times 10^7$	8.29	7.30	36
I ⁻	$1.49 (\pm 0.55) \times 10^7$	8.36	7.42	36

^a According to eq 17. ^b According to eq 13 and either eq 15 or 16; see text. ^c Parentheses contain one standard deviation in bimolecular rate constant. ^d Sources for nucleophilicities for S_N2 displacement of I⁻ from methyl iodide in methanol.

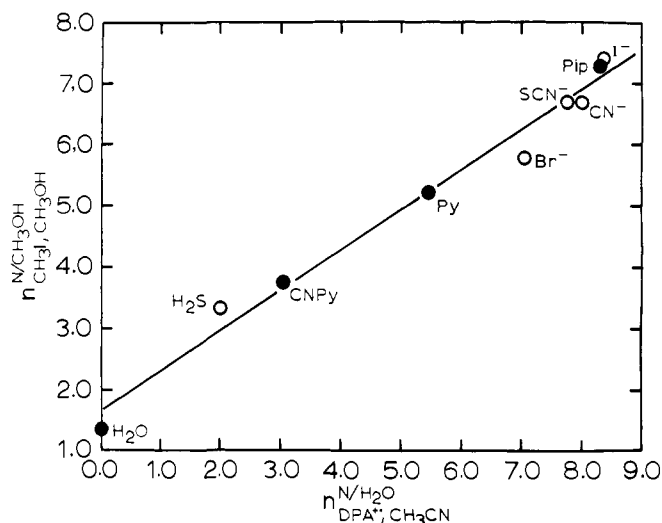


Figure 1. Correlation of nucleophilicity parameters (eq 17) for DPA⁺ reactions with those for S_N2 displacement of iodide from methyl iodide. Solid circles are for reactions of DPA⁺, in which addition products are observed; open circles are for those in which electron transfer products are noted. Coefficient of correlation = 0.991.

$$k = k_{\text{obsd}} \quad (16)$$

Following the approach of Swain and Scott¹⁹ in the definition of a nucleophilicity parameter, n , we choose to designate solvent system (S), substrate (SUB), and reference nucleophile (M) for a given nucleophile (N) such that

$$n_{\text{SUB}, \text{S}}^{\text{N}/\text{M}} = \log(k_{\text{N}}/k_{\text{M}}) \quad (17)$$

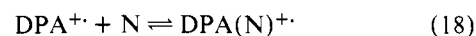
where k_{N} is the elementary bimolecular rate constant for the reaction of N with SUB, and, likewise, k_{M} is the elementary bimolecular rate constant for the reaction of M with SUB. Accordingly, the kinetic data for the DPA⁺/nucleophile reactions reported here, in which the rate law given by eq 13 applies, yields the nucleophilicity parameters given in Table IV. Included in the table are the nucleophilicities for the S_N2 displacement of iodide from methyl iodide in methanol. Our parameters employ the hydrolysis of the DPA cation radical (slowest case found) as the reference reaction, vis-à-vis the solvolysis reference reaction for the methyl iodide reactions.^{19,36}

A plot of nucleophilicities toward DPA⁺ in acetonitrile vs. nucleophilicities toward methyl iodide in methanol shows the striking correlation depicted in Figure 1. That this correlation for nine different nucleophiles is not simply fortuitous is indicated by its linearity over nine orders of magnitude of reactivity toward DPA⁺. If a common transition state were formed in both the addition and the electron transfer reactions of these nucleophiles with DPA⁺, then a correlation with the integrity

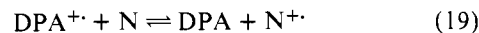
shown in Figure 1 could be expected. If this were the case, then it becomes necessary to discuss the ramifications of such a common transition state in light of the data available from these and other rate measurements involving nucleophilic attack on various substrates. Let us examine two extreme models for this common transition state.

In one extreme, consider that all reactions of DPA⁺ involve a transition state in which the nucleophile (or reducing agent) is in the process of displacing a highly interactive solvent molecule (acetonitrile) from a reactive site of DPA⁺, the 9 or 10 position.³⁷ The approach of these reactants toward this transition state is envisioned to involve nearly complete desolvation of the nucleophile en route to attainment of a transition state of structure similar to those described for S_N2 displacement.³⁸ That is, DPA⁺ remains strongly solvated by a molecule of acetonitrile in the transition state.

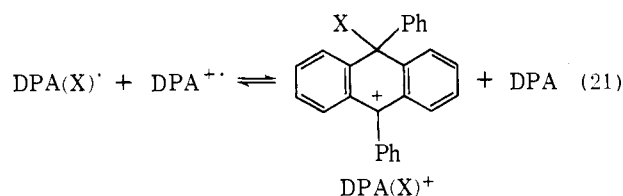
How then do electron transfer products result from a transition state in which a substantial degree of bonding between the reducing agent and DPA⁺ has been achieved? There are at least two possible routes which may account for the observation of both electron transfer and addition product types. One possibility would involve completion of bond formation with expulsion of solvent to yield the cation radical/nucleophile adduct (DPA(N)⁺)

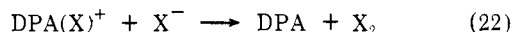


which ultimately gives rise to an addition product; or, alternatively, this transition state, following transfer of an electron from "nucleophile" to DPA⁺, would dissociate into DPA and the oxidized form of the nucleophile (N⁺).



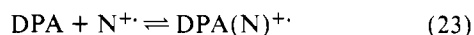
From these considerations, the type of reaction products observed would depend largely on the relative stability of the products of the initial encounter of DPA⁺ and nucleophile (i.e., DPA(N)⁺ vs. DPA + N⁺). A second possibility is that the completion of bond formation may take place in both addition and electron transfer reactions such that for the reactions in which DPA is completely regenerated (electron transfer cases), a modified form of Scheme I (half-regeneration mechanism) may be invoked; namely, for the case of a negatively charged nucleophile, eq 20–22. This proposition is consistent with (1)





kinetic evidence for a $\text{DPA}(\text{X})^+$ species in the DPA^+/Cl^- reaction¹⁷ and (2) species such as $\text{DPA}(\text{X})^+$ have long been proposed as intermediates in electrophilic aromatic substitution.^{39,40} In this context, it is the relative stability of the possible products ($\text{DPA} + \text{X}_2$ vs. $\text{DPA}(\text{N})_2^{2+}$) which may result from attack of a second nucleophile (X^- or N) on the oxidized form of the cation radical/nucleophile adduct ($\text{DPA}(\text{X})^+$ or $\text{DPA}(\text{N})_2^{2+}$) which determines whether or not an addition product is obtained.

In the other extreme, a common transition state model of the "electron transfer" type may be envisioned. Here, the closest approach of nucleophile and DPA^+ may be considered less than that in the model discussed above, such that there is very little orbital overlap, if any, between these reactants in the activated complex. One may view this activated complex in a nonequilibrium sense, as explicated by Marcus.⁴¹ Along these lines, all of the DPA^+ /nucleophile reactions may be considered to involve rate-determining electron transfer between reactants (eq 19). Addition products then result from subsequent coupling of the products of the initial electron transfer step



in a fashion analogous to that described by House for nucleophilic addition to organocuprate systems.⁴² Electron transfer product types are obtained when combination of two oxidized nucleophiles (halide and pseudohalide cases)



or further oxidation of oxidized nucleophile (H_2S case)¹⁶



by a second DPA^+ is more energetically favorable than the coupling of oxidized nucleophile and neutral DPA .

The data presented here do not permit the clear choice of one of these models as the more accurate description of the *postulated* common transition state in the DPA^+ /nucleophile systems studied. Rather, these results suggest further work in which the kinetic behavior of intermediates (e.g., $\text{A}(\text{N})^+$) and products (e.g., X_2 , X_3^-) is examined. There are, however, certain indications here that the electron transfer-like model may be more appropriate if indeed a common transition state is extant in the systems discussed herein. It should be noted that the reactivity order of I^- more reactive than Br^- toward DPA^+ is reversed from that expected for $\text{S}_{\text{N}}2$ displacement reactions in an acetonitrile medium where solvation of these nucleophiles is weak (cf. dipolar aprotic solvents³⁸ and molten salt systems⁴³). Indeed, the correlations of Edwards⁴⁴ indicate that even in classical $\text{S}_{\text{N}}2$ reactions, nucleophilic reactivity is predominantly attributable to an electrochemical parameter, so that the proposition of an electron transfer-like transition state for all reactions of nucleophiles may well be reasonable in light of the correlation shown in Figure 1. In this context, perhaps the concept of treating the electron as a nucleophile as discussed by Kojima et al.⁴⁵ is also fundamental to an understanding of nucleophilic reactivity. The free-energy change associated with electron transfer from nucleophile to electrophile may then be considered to be the key parameter in determining nucleophilicity. The products observed for a given reaction are then dictated by the relative thermodynamics and/or kinetics of the various association pathways available to the oxidized nucleophile and reduced electrophile (eq 23 and 24).

Conclusions

From the data presented here, there is clear indication that, for reactions of DPA^+ with various nucleophiles, both product

type (addition vs. electron transfer) and relative reaction rate (for both reaction types) may be predicted from a knowledge of oxidation potential of the nucleophile and $\text{S}_{\text{N}}2$ nucleophilicity parameters, respectively. Moreover, for those reactions in which the nucleophile undergoes addition to DPA^+ , the half-regeneration mechanism is found to account for the observed reaction dynamics in all such cases.

The correlation between nucleophilic reactivities found for both the addition and the electron transfer reactions of DPA^+ with these nucleophiles and the nucleophilicities for $\text{S}_{\text{N}}2$ substitution at tetrahedral carbon suggests a certain degree of inseparability of redox reactivity and nucleophilic reactivity toward electron-deficient systems. There have been other systems which bear out this suggestion in that nucleophilic addition products may arise from electron transfer from nucleophile to substrate followed by coupling of the oxidized form of the nucleophile and the reduced form of the substrate.⁴² The considerations presented here suggest that a rethinking of nucleophilic reactivity in terms of electron transfer theory *may afford* an enhanced understanding of the factors which govern reactivity in nucleophilic addition reactions.

Experimental Section

Materials. Acetonitrile (UV grade) used in all studies reported here was obtained from Burdick and Jackson Laboratories (Muskegon, Mich.) and further purified as previously described.⁴⁶ DPA (Aldrich "Gold Label") was twice recrystallized from absolute ethanol, mp 251–252 °C. Tetra-*n*-butylammonium perchlorate (TBAP) was obtained from Eastman and twice recrystallized from acetone–water (15:85) and vacuum dried at 60 °C for 6 h,⁴⁷ mp 211.5–212.5 °C.

All halide and pseudohalide nucleophiles were introduced into reaction media as their respective tetraalkylammonium salts. Tetra-*n*-butylammonium bromide (TBABr, Eastman) was twice crystallized from absolute ethanol by the addition of anhydrous ether and dried in vacuo (80 °C, 6 h), mp 118–119.5 °C (lit.⁴⁸ 118.5 °C). Tetra-*n*-butylammonium iodide (TBAI, Eastman) was doubly recrystallized from distilled, deionized water and dried in vacuo (60 °C, 6 h), mp 145.5–147 °C (lit.⁴⁹ 146 °C). Tetra-*n*-butylammonium thiocyanate (TBASCN) was isolated from the metathesis of equimolar acetone solutions of KSCN and TBABr,⁵⁰ twice crystallized from acetone by the addition of anhydrous ether, and vacuum dried (70 °C, 24 h), mp 123.5–125 °C. Tetraethylammonium cyanide (TEACN) was prepared by the metathesis of methanolic solutions of NaCN and tetraethylammonium chloride⁵¹ and recrystallized from acetonitrile. Acetonitrile stock solutions were immediately prepared from this material.

Pyridine (J. T. Baker) was purified as detailed elsewhere.¹ CNpy (Aldrich) was twice recrystallized from benzene, mp 79.0–79.5 °C. Et_3N (Eastman) was fractionally distilled from KOH at atmospheric pressure and the fraction boiling at 88–89 °C retained. Pip (MCB) was purified in like manner, the retained fraction boiling at 105–105.5 °C.

All solution preparations were carried out in a nitrogen-filled drybox. TBAP was present at 0.10 M concentration in spectroelectrochemical experiments as both a supporting electrolyte and the determinant of ionic strength. In stopped-flow work, TBAP (0.10 M) was present in both cation radical and nucleophile solutions for control of ionic strength and for elimination of thermal perturbations during mixing.¹⁷

Concentrations of DPA , TBAP, TBABr, TBAI, TBASCN, and CNpy were determined by direct weighings and subsequent serial dilutions. The concentrations of the TEACN stock solutions described above were determined by potentiometric titration with AgNO_3 . The concentrations of Et_3N , py, and Pip in stock acetonitrile solutions were determined by potentiometric titrations with HClO_4 . Serial dilutions of these stock solutions afforded the desired concentrations of the respective nucleophile.

Apparatus. Kinetic studies were conducted at 25.0 (± 0.5) °C using spectroelectrochemical (SE)⁵² and stopped-flow (SF)^{16,17} techniques. SE measurements were made using platinum optically transparent electrodes (OTE)⁵³ fitted to cells of a previously reported design.⁵⁴ In all cases, single-beam transmission configurations were employed.⁵² Potential step perturbations were applied to these OTEs via a three-

electrode potentiostat equipped with circuitry for compensation of solution resistance.⁵⁵ All electrode potentials are reported relative to the aqueous saturated calomel electrode. The closed system utilized for electrogeneration of DPA⁺ and its transfer to the Durrum D-110B stopped-flow spectrophotometer has been described elsewhere.^{16,17} In both SE and SF, the kinetic spectrophotometers employed were interfaced to a dedicated computer system for the acquisition, reduction, and presentation of data.^{1,14,16,17} Assignments of reaction order and extraction of attendant kinetic parameters were carried out by regression analysis.

Product Characterizations. Regeneration of precursor (DPA) from reactions of DPA⁺ with excess nucleophiles was monitored spectrophotometrically in the stopped-flow apparatus at 392.5 nm,^{9,16,17} where no other species interfered with this determination. Following reaction between DPA⁺ and TBAI, absorption maxima at 292.0 and 362.5 nm indicated the presence of periodide. The reaction of DPA⁺ with TBASCN gave rise to a yellow oil identified as parathiocyanogen, (SCN)_x, by comparison of its infrared spectrum with that of authentic (SCN)_x prepared by the exhaustive mono-electronic oxidation (Pt anode, $E_{\text{applied}} = 1.20$ V) of acetonitrile solutions of TBASCN.^{56,57} In both cases the yellow oils obtained exhibited infrared spectra with absorption maxima at 2060 and 1610 cm⁻¹ in good agreement with the reported values.⁵⁷

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$$n_{\text{CH}_3\text{I,CH}_3\text{OH}}^{\text{N/CH}_3\text{OH}} = 1.14 (n_{\text{CH}_3\text{I,H}_2\text{O}}^{\text{N/H}_2\text{O}}) + 1.35$$
 and yields values of 1.35 and 6.01 for N = H₂O and N = OH⁻, respectively. The value of $n_{\text{CH}_3\text{I,CH}_3\text{OH}}^{\text{H}_2\text{S/CH}_3\text{OH}}$ is then estimated according to

$$k_{\text{SH}^-}/k_{\text{OH}^-} = k_{\text{H}_2\text{S}}/k_{\text{H}_2\text{O}}$$
- or

$$n_{\text{CH}_3\text{I,CH}_3\text{OH}}^{\text{H}_2\text{S/CH}_3\text{OH}} = n_{\text{CH}_3\text{I,CH}_3\text{OH}}^{\text{H}_2\text{O/CH}_3\text{OH}} + n_{\text{CH}_3\text{I,CH}_3\text{OH}}^{\text{SH}^-/\text{CH}_3\text{OH}} - n_{\text{CH}_3\text{I,CH}_3\text{OH}}^{\text{OH}^-/\text{CH}_3\text{OH}} = 3.34$$
 where $n_{\text{CH}_3\text{I,CH}_3\text{OH}}^{\text{SH}^-/\text{CH}_3\text{OH}}$ is given by Pearson et al.³⁶ as 8.
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