

provides the best correlation for singlet CH₂ described as a GVB(1/2) orbital pair. (The CH₂ σ pair at R_e(Cr-C) prefers a σ -correlating orbital.)

We now discuss the CI's in terms of their dissociation limits.

(1) GVB(1/2)-PP and GVB-RCI(2) both dissociate to Hartree-Fock (HF) Cr⁺ (total energy = -1042.004 30 hartree) and GVB(1/2)CH₂ (total energy = -38.901 64 hartree). [We calculate an HF bond energy by dissociating to HF Cr⁺ and HF CH₂ (total energy = -38.880 98 hartree).]

(2) RCI(2)*D_o dissociates to HF Cr⁺ and RCI(2)*D_o CH₂ (total energy = -38.916 49 hartree; 45 spatial configurations/45 spin eigenfunctions).

(3) RCI(2)*S_{val} dissociates to HF*S_{val} Cr⁺ (equivalent to HF here) and RCI(2)*S_{val} CH₂ (total energy = -38.907 64 hartree; 34 spatial configurations/37 spin eigenfunctions). The RCI*S_{valence} CI in general not dissociation-consistent, but due to the equivalence of HF to HF*S for d⁵ Cr⁺, this CI, as are all the ones discussed here, is indeed dissociation-consistent.¹

(4) RCI(2)*S_{val} + RCI(2)*D_o dissociates to HF (or equivalently, HF*S_{val}) Cr⁺ and [RCI(2)*S_{val} + RCI(2)*D_o] CH₂ (total energy = -38.922 49 hartree; 69 spatial configurations/72 spin eigenfunctions),

since the σ bond localizes back on CH₂ at R = ∞ .

E. State Splittings. In order to preserve a balanced description of the ⁶A₁ and ⁴B₁ states of CrCH₂⁺, we must allow the same degree of freedom for both states in order to ensure we are treating both states equivalently (no artificial biases). We can accomplish this by maintaining the same number of occupied orbitals included in the SCF description of both states. The ⁶A₁ state, with a GVB(1/2) description, has a valence space consisting of two C-H doubly occupied orbitals (treated as HF MO's), one Cr-C bond pair with two natural orbitals (NO's), and five singly occupied nonbonding 3d-orbitals, for a total of nine orbitals in the valence space. The ⁴B₁ state, with a GVB(2/4) description, has a valence space consisting of the two C-H HF MO's, two Cr-C bond pairs (four NO's), and three singly occupied 3d-orbitals, for a total of nine orbitals again. Therefore we have a balanced orbital description of the two states at the two levels described above.

F. Ru Carbene Calculations. All calculations on the various electronic states of RuCH₂⁺ are described in paper 2 of this series.^{1b}

Acknowledgment. Partial support of this work is gratefully acknowledged from the Shell Development Co., Houston, TX, and the National Science Foundation (Grant CHE83-18041).

Electrochemically Catalyzed Aromatic Nucleophilic Substitution. Reactivity of Cyanide Ions toward Aryl Radicals in Liquid Ammonia

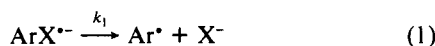
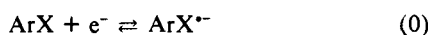
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Received January 6, 1986

Abstract: The mechanism of the substitution of a series of aromatic halides by cyanide ion under electrochemical induction is described as a function of the substrate. The rate constants of the addition of cyanide ion on eight aryl radicals have been determined by using either a direct or a competitive electrochemical method. The variation of the reactivity toward the CN⁻ ions with the structure of the aryl radicals is discussed.

Aromatic nucleophilic substitution occurring along a S_{RN1} mechanism^{2a} has been the object of active attention during the past 15 years.^{2,3} It proceeds along the following reaction sequence:



and/or



thus requiring an electron transfer reduction (the source of electron being an electrode,³ solvated electrons,² or other redox reagents⁴) or a photoreduction² of the substrate ArX. Cleavage of the anion radical, ArX^{•-}, thus generated produces the σ -aryl radical, Ar[•], which is the actual electrophilic reactant in the reaction rather than the starting ArX. The key step of the reaction is then the coupling of the aryl radical and the nucleophile, leading to the

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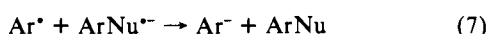
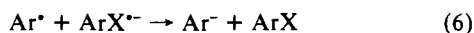
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Table I. Rate Constants of the Reaction of Cyanide Ion^a with Aryl Radicals in Liquid NH₃ at -40 °C^b

Ar ^c	X	working electrode	supporting ^e electrolyte	k ₂ , M ⁻¹ s ⁻¹	E ^o _{ArCN/ArCN⁻} ^f
phenyl	Cl	Au	KBr	≤4 × 10 ⁵	-1.78
	SPh		KBr		
1-naphthyl	Cl	Au	KBr	10 ⁶	-1.375
2-cyanophenyl ^d	Cl	Pt	KBr	9.5 × 10 ⁸	-1.13
3-cyanophenyl	Cl	Au	NaI	5 × 10 ⁷	-1.20
4-cyanophenyl ^d	Br	Au	KBr	3.5 × 10 ⁷	-1.05
	Cl			2.7 × 10 ⁷	
2-quinolyl	Br	Hg	NaI	≤2 × 10 ⁶	~-0.95 ^g
4-benzoyl ^e	Br	Hg	KBr	4.5 × 10 ⁷	-0.88
4-quinolyl	Cl	Hg	NaI	3 × 10 ⁸	-0.815

^a Introduced in the solution as the sodium salt. ^b Determined by the direct electrochemical method unless otherwise stated. ^c Concentration, 0.1 M. ^d Determined by the electrochemical competition method (competition with diethyl phosphite ions). ^e From ref 3. ^f In V vs. Ag/0.01 M Ag⁺. ^g Rough estimation from the value for 4-cyanoquinoline and the E^o's for quinoline substituted in the 2- and 4-positions by -SPh and -P(O)(OEt)₂ (Table VI in ref 3g).

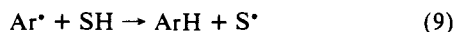
anion radical of the target substituted product, ArNu⁻. This species is then reoxidized into the final product, ArNu, the oxidant being any electron sink present in the reaction medium, e.g., an electrode or the substrate itself. In the latter case, the reaction occurs along a chain mechanism. It thus appears that only a catalytic amount of electrons is required for the reaction to proceed. The above reaction mechanism was put forward on the basis of the stimulation role of electrons injected in the system under the form of an alkali metal dissolved in liquid ammonia^{2a} and of the inhibition of the reaction by radical scavengers.^{2b} Electrochemistry³ has provided a clear demonstration of the above reaction mechanism, showing that the electrochemical catalysis of the substitution reaction requires an electrode potential where ArX is reduced and that the overall kinetics of the process as measured by the current flowing through the electrode fits what is predicted from the above reaction scheme. As to the latter point, it is noteworthy that not only the steps listed below must be taken into account but also a series of side reactions deactivating the aryl radicals toward the addition of the nucleophile. In the first place, these side reactions are electron transfers taking place at the electrode surface or in the solution



yielding the aryl carbanion which is rapidly protonated by the solvent or by residual water



leading to the hydrogenolysis hydrocarbon, ArH, as a side product vis-à-vis the substitution product. These are the main side-reactions competing with the substitution process in solvents, such as liquid ammonia, that are poor H-atom donors.^{3a,5} In the organic solvents commonly used in organic electrochemistry such as dimethyl sulfoxide and acetonitrile, an additional side reaction takes place, viz., the abstraction of a hydrogen atom from the solvent by the aryl radicals:



(S[•] is further reduced at the electrode or in the solution).^{3d} Note that in the cases when the substitution reaction is a chain process, by means of eq 4, the side reactions just described function as termination steps vis-à-vis the chain process.^{3b}

The coupling between the aryl radicals and the nucleophile (reaction 2) appears as the key step of the S_{RN1} reaction. It is thus of interest to determine its rate constant as a function of the structure of the aryl radical and of the nucleophile, in an attempt

to sketch a structure-reactivity relationship characteristic of the S_{RN1} reaction. After a few sparse determinations^{3a-f,5} more systematic investigations of this problem have been undertaken recently. Relative rate constants of a series of nucleophiles including Ph₂P⁻, Ph₂PO⁻, (EtO)₂PO⁻, Me₃CCOCH₂⁻, and PhS⁻, toward the phenyl radical have been derived from the ratio of the substitution products obtained upon reaction of iodobenzene with pairs of nucleophiles under photochemical stimulation.^{2c} Relative but also absolute rate constants have been more recently measured from three nondestructive electrochemical methods based on the analysis of the systems by cyclic voltammetry in a series including 10 aryl radicals and three nucleophiles (PhS⁻, (EtO)₂PO⁻, CH₃COCH₂⁻) in liquid ammonia.^{3g,h}

The purpose of the work reported hereafter was to complete this series of measurements in liquid ammonia, with another nucleophile, the cyanide ion. Among the large number of nucleophiles that have been tested in aromatic S_{RN1} reactions,^{6a} cyanide ions suffer a bad reputation,^{6b} although it was shown to react under electrochemical stimulation with nitrophenyl radicals in Me₂SO,^{7a} 4-benzoyl, and 1-naphthyl radicals in acetonitrile^{3b,7b} and 4-benzoyl radicals in liquid NH₃.^{3f} It will be seen that the rate constants of the reaction of CN⁻ with these aryl radicals and a series of others can be determined electrochemically. As shown previously, in most cases the rate constants for the reaction of the three nucleophiles, PhS⁻, (EtO)₂PO⁻, and CH₃COCH₂⁻, are practically at the diffusion limit precluding the determination of their actual reactivity.^{3g} One interesting feature of cyanide ion as a nucleophile is that the rate constants are well below the diffusion limit in all cases.

Results

The direct electrochemical method was used in all cases with the exception of the 2- and 4-cyanophenyl radicals for which the competition electrochemical method^{3h} was employed. In the absence of the nucleophile, the cyclic voltammogram of the substrate exhibits a two-electron irreversible wave which features the reaction sequence involving reactions 0, 1, 5 and/or 6 and 8. A second one-electron wave is usually observed, corresponding to the reduction of ArH formed at the first wave. Addition of the nucleophile results in a decrease of these two waves and in the appearance of a new wave corresponding to the reduction of the substituted product ArCN. This can be located either in front or beyond the ArX wave. The direct method consists in measuring the height of the first wave, *i*_p, normalized with respect to the peak height obtained in the absence of the nucleophile,⁸ as a function of the nucleophile concentration. The use of previously established theories^{5b,3g} relating *i*_p/*i*_p⁰ to the rate constant *k*₂ then allowed the derivation of *k*₂ from the experimental data. In most cases, ArX was the aryl chloride with the exceptions listed in Table I.

(6) (a) For a review, see ref 2g. (b) See p 260 in ref 2g.

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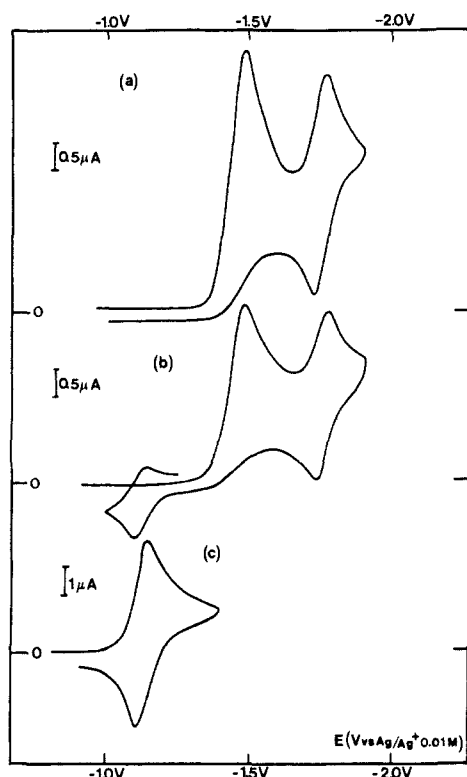


Figure 1. Cyclic voltammetry of 2-chlorobenzonitrile (1.95 mM) in liquid $\text{NH}_3 + 0.1 \text{ M KBr}$ at -40°C in the absence of CN^- ions (a) and in the presence of 1.5 M NaCN (b). Cyclic voltammetry of phthalonitrile (2.7 mM) in the same conditions (c). Sweep rate, 0.115–0.2–0.38 V s^{-1} .

Another quantity of interest is the standard potential of the $\text{ArCN}/\text{ArCN}^{\cdot-}$ redox couple. It can be directly measured on the cyclic voltammograms when $\text{ArCN}^{\cdot-}$ is chemically stable. As discussed below, problems were encountered in this connection in some cases where the $\text{ArCN}^{\cdot-}$ anion radicals tend to dimerize.

2-Chlorobenzonitrile, 4-bromobenzonitrile, and 4-chloroquinoline exhibit similar behaviors in cyclic voltammetry upon addition of cyanide ions in the solution. Figure 1 shows a typical cyclic voltammogram obtained with **2-chlorobenzonitrile** in the absence and presence of cyanide ions. In the absence of CN^- , two waves are observed. The first two-electron irreversible wave corresponds to the reductive cleavage of the C–Cl bond yielding benzonitrile. The second one-electron reversible wave corresponds to the reduction of benzonitrile into its anion radical which is stable within the time scale of the experiments even at low sweep rates. Upon addition of CN^- to the solution, these two waves decrease and a new reversible wave appears at a more positive potential. The latter is identical with the one-electron reversible wave of an authentic sample of phthalonitrile (*o*-dicyanobenzene),^{3b} showing that the chloride ion has been substituted by a cyanide ion.

With **4-bromobenzonitrile**, the new reversible wave appearing similarly in front of the 4-bromobenzonitrile waves is likewise identical with the reversible wave of an authentic sample of the substitution product, terephthalonitrile.

In the case of **4-chloroquinoline**, which exhibits the same behavior, we can thus infer that the reversible wave appearing in front of the initial waves upon addition of CN^- is also that of the substitution product, although an authentic sample of this was not available. The rate constant k_2 was determined by the direct method with this compound from the decrease of the peak current, i_p , of the two-electron irreversible wave upon addition of CN^- ions. Since the cleavage rate constant of the initial anion radical, $\text{ArX}^{\cdot-}$, is large ($9.5 \times 10^6 \text{ s}^{-1}$),⁹ it is expected that the oxidation of the $\text{ArCN}^{\cdot-}$ anion radical and the reduction of Ar^* will both occur at the electrode surface rather than in the solution, i.e., will proceed

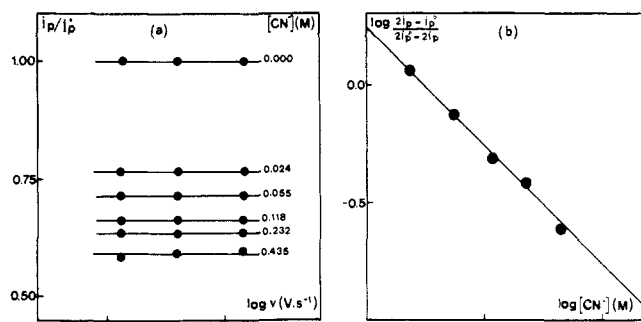


Figure 2. Cyclic voltammetry of 4-chloroquinoline (2.3 mM) in liquid $\text{NH}_3 + 0.1 \text{ M NaI}$ at -40°C . Variations of the normalized peak height of the first wave, i_p/i_p^0 , with sweep rate and CN^- concentration (a). Characteristic function of an ECE-substitution noncatalytic mechanism (b) (see text).

according to steps 3 and 5, respectively.¹⁰ In other words, the reaction sequence corresponds to an ECE-substitution “noncatalytic” competition scheme, “ECE” because the second electron transfer predominantly takes place at the electrode surface, noncatalytic because, at the level of the ArX wave, the minimal number of electrons per molecule is one since the standard potential of the $\text{ArNu}/\text{ArNu}^{\cdot-}$ couple is positive to that of the $\text{ArX}/\text{ArX}^{\cdot-}$ couple.^{5b} The corresponding theory^{5b} then indicates that the relative decrease of the peak current should be expressed as

$$\log \frac{2i_p - i_p^0}{2i_p^0 - 2i_p} = -\frac{1}{2} \log [\text{CN}^-] + \frac{1}{2} \log \frac{k_1}{k_2}$$

i.e., be a function of the cyanide ion concentration but not of the sweep rate and the ArX concentration. As seen in Figure 2, this is what is observed experimentally, the slope toward $\log [\text{CN}^-]$ being $1/2$, as expected. The rate constants ratio k_1/k_2 ensues ($3 \times 10^{-2} \text{ M}$) and thus k_2 (Table I) since k_1 ($9.5 \times 10^6 \text{ s}^{-1}$)⁹ is known from previous experiments.

The comparative method was used in the case of **2-chlorobenzonitrile** and **4-bromobenzonitrile**. Typical repetitive steady-state cyclic voltammograms obtained with 2-chlorobenzonitrile and 4-bromobenzonitrile in the presence of mixtures of cyanide and diethyl phosphite ions are shown in Figures 3 and 4, respectively.¹¹ As expected the ratio of the two peaks is proportional to the concentration ratio of the two nucleophiles. The ratio of the rate constants between cyanide and diethyl phosphite ions ensues: 0.12 for the 2-cyanophenyl radical, 0.023 for the 4-cyanophenyl radical. Using the k_2 values previously determined for $(\text{OEt})_2\text{PO}^{\cdot-}$,^{3h} one obtains the values reported in Table I for CN^- .

When CN^- ions are added to a solution of **4-chlorobenzonitrile**, a small but definite decrease of the peak height of the first two-electron irreversible wave results. This appears to be independent of the sweep rate as in the case of 4-chloroquinoline which falls in line with an ECE-substitution reaction scheme as expected

(10) The competition between the heterogeneous and homogeneous second electron transfers is governed by the parameter $(k_D[\text{ArX}]/k_1^{3/2})(Fv/RT)^{1/2}$ where k_D is the rate constant of the homogeneous electron transfer, k_1 the cleavage rate constant of $\text{ArX}^{\cdot-}$ and v the sweep rate. When the parameter is small, heterogeneous electron transfer prevails and vice versa. Assuming that k_D is at the diffusion limit ($3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), for $v = 0.1 \text{ V s}^{-1}$ and $[\text{ArX}] = 1 \text{ mM}$, reduction of Ar^* occurs equally at the electrode surface and in the solution for $k_1 \approx 2 \times 10^5 \text{ s}^{-1}$.

(11) More precisely, the experiments were carried out in the presence of a constant concentration of $(\text{OEt})_2\text{PO}^{\cdot-}$ (20 mM) introducing increasing amounts of CN^- . The steady-state cyclic voltammogram in the presence of 20 mM $(\text{OEt})_2\text{PO}^{\cdot-}$, without CN^- added, only shows the wave of the substituted product. This is not the case in the presence of CN^- alone, where the waves of ArX are still seen even at high CN^- concentrations. In the presence of a mixture of the two nucleophiles only the reversible waves of the two substitution product are seen. This is simply explained by noting that the chain propagation reaction (4) is fast with $(\text{OEt})_2\text{PO}^{\cdot-}$ (downhill reaction) and slow with CN^- (uphill reaction).

(9) Due to a material error the value reported for k_1 in ref 3 g is not correct. It should be read 9.5×10^6 instead of $1.9 \times 10^6 \text{ s}^{-1}$.

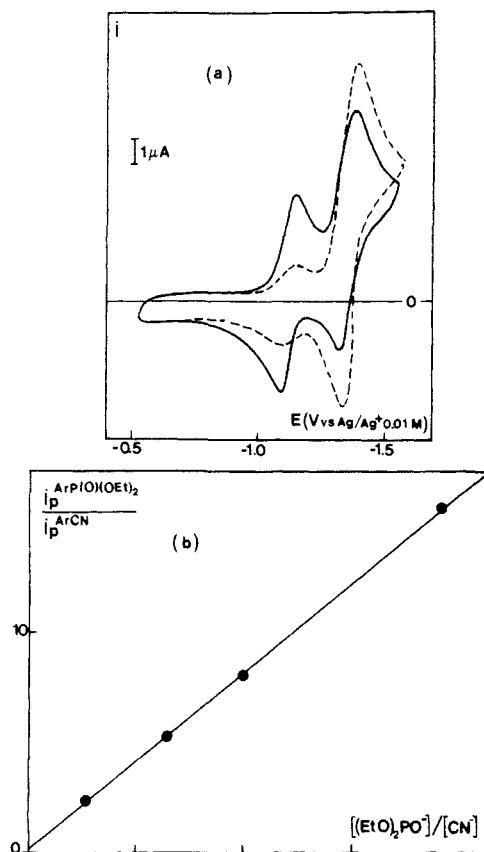


Figure 3. Repetitive cyclic voltammetry of 2-chlorobenzonitrile (2 mM) in liquid $\text{NH}_3 + 0.1 \text{ M KBr}$ at -40°C in the presence of mixtures of $\text{OP}(\text{OEt})_2^-$ and CN^- ions. (a) Cyclic voltammograms with 20 mM $\text{OP}(\text{OEt})_2^-$ and 20 mM CN^- (---) and 167 mM CN^- (—). (b) Ratio of the two cathodic peaks as a function of the concentration ratio of the two nucleophiles. The first and second peaks are those of the cyano and diethyl phosphite derivatives, respectively. The height of the second peak is measured from the extension of the first. Sweep rate, 0.38 V s^{-1} .

from the large value of k_1 ($9.3 \times 10^8 \text{ s}^{-1}$).³⁸ From this, an approximate value of k_2 , $2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, can be derived which is in good agreement with the value obtained from the application of the comparative method to 4-bromobenzonitrile.

Another example where the dimerization of the anion radical of the cyano-substituted product does not interfere is that of **4-bromobenzophenone**. Upon addition of cyanide ions, the reversible wave of 4-cyanobenzophenone again appears in front of the waves of 4-bromobenzophenone while its first irreversible two-electron wave decreases. The variations of the peak height in the presence of cyanide ions are, however, different from the case of 4-chloroquinoline. i_p/i_p^0 is independent from the sweep rate but depends upon the concentration ratio $[\text{CN}^-]/[\text{ArX}]$ which corresponds to a different reaction mechanism. Owing to the fact that the cleavage of the $\text{ArX}^{\cdot-}$ anion radical is now slow (600 s^{-1}),¹² the electron-transfer reactions following the initial electron transfer at the electrode, reaction 0, and the cleavage of the resulting anion radical, reaction 1, now occur in the solution. Since the $\text{ArCN}/\text{ArCN}^{\cdot-}$ couple is located at a standard potential well positive to that of the $\text{ArX}/\text{ArX}^{\cdot-}$ couple, reaction 4 proceeds from right to left with a rate constant close to the diffusion limit (k_D). It follows that the side reaction consuming the Ar^{\cdot} radical is predominantly (7) instead of (6). Under these conditions, i_p/i_p^0 is a function of the dimensionless parameter $\epsilon = k_D[\text{ArX}]/k_2[\text{Nu}^-]$. The formal kinetics featuring this reaction mechanism have been analyzed in detail elsewhere and the reduction of 4-bromobenzophenone in the presence of CN^- anions has been taken as a typical illustrative example.^{3f} The rate constant k_2 reported

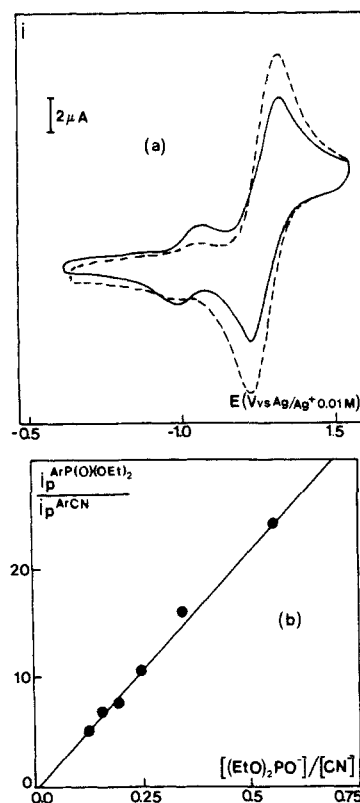


Figure 4. Repetitive cyclic voltammetry of 4-bromobenzonitrile (2.2 mM) in liquid $\text{NH}_3 + 0.1 \text{ M KBr}$ at -40°C in the presence of mixtures of $\text{OP}(\text{OEt})_2^-$ and CN^- ions. (a) Cyclic voltammograms with 20 mM $\text{OP}(\text{OEt})_2^-$ and 38 mM CN^- (---) and 130 mM CN^- (—). (b) Ratio of the two cathodic peaks as a function of the concentration ratio of the two nucleophiles. The first and second peaks are those of the cyano and diethyl phosphite derivatives, respectively. The height of the second peak is measured from the extension of the first. Sweep rate, 0.5 V s^{-1} .

in Table I resulted from the treatment of the experimental data according to this reaction scheme.

3-Chlorobenzonitrile is a typical example where the dimerization of the anion radical of the substitution product, isophthalonitrile, interferes. Unlike the anion radicals of phthalonitrile and terephthalonitrile, the anion radical of isophthalonitrile is known to dimerize in DMF at room temperature.¹³ The same happens in liquid ammonia as suggested by the following observations. As cyanide ions are added to the solution, the peak height of the first two-electron irreversible wave decreases but no wave corresponding to the isophthalonitrile/isophthalonitrile anion radical couple appears at a more positive potential, at least in the $0.1\text{--}0.5 \text{ V s}^{-1}$ sweep rate range (Figure 5a,b). This, however, shows up upon cycling the potential repetitively over the ArX wave at 20 V s^{-1} . It is located at a standard potential of $-1.20 \text{ V vs. Ag}/\text{Ag}^+ 0.01 \text{ M}$. The cyclic voltammogram of isophthalonitrile itself is shown in Figure 5c. At low sweep rates a 1e irreversible wave is observed. It becomes reversible at high sweep rate (600 V s^{-1} for a concentration of 3–9 mM), similarly to what happens in DMF. The anodic wave observed upon scan reversal can thus be ascribed to the reoxidation of the dimer dianion formed at the cathodic wave. This is also similar to what was found with 1-cyanonaphthalene as described in more details below. When 3-chlorobenzonitrile is added to the isophthalonitrile solution in the presence of CN^- ions, it is observed (Figure 5d) that the anodic wave increases confirming the formation of the dimer-dianion of isophthalonitrile as a result of the electrochemically induced $\text{S}_{\text{RN}}1$ substitution of Cl by CN . Since the cleavage rate of the 3-chlorobenzonitrile anion radical is large ($k_1 = 10^6 \text{ s}^{-1}$),^{3h} the reaction proceeds in

(13) (a) Rieger, P. H.; Bernal, I.; Reinmuth, W. H.; Fraenkel, G. K.; *J. Am. Chem. Soc.* **1963**, *85*, 683. (b) Gennaro, A.; Romanin, A. M.; Severin, M. G.; Vianello, E. *J. Electroanal. Chem.* **1984**, *169*, 219. (c) Gennaro, A.; Maran, F.; Maya, A.; Vianello, E. *J. Electroanal. Chem.* **1985**, *185*, 353.

(12) Savéant, J. M.; Thiébaud, A. *J. Electroanal. Chem.* **1978**, *89*, 335.

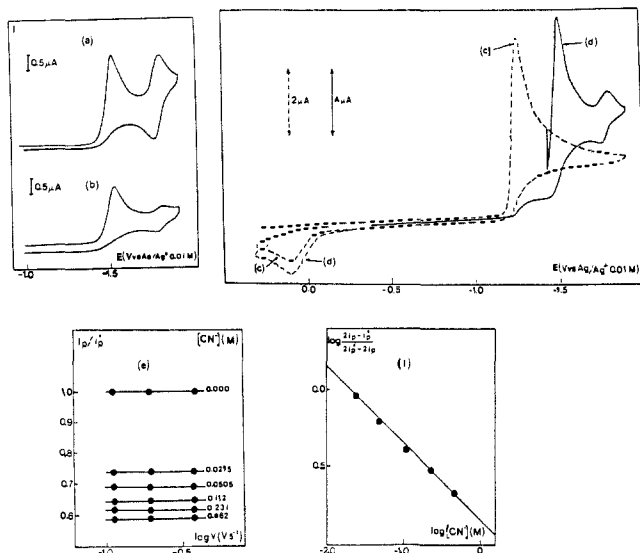


Figure 5. Cyclic voltammograms of 3-chlorobenzonitrile (1.1 mM) in liquid $\text{NH}_3 + 0.1 \text{ M NaI}$ at -40°C as a function of the CN^- concentration. (a) Cyclic voltammogram without CN^- ions ($\nu = 0.2 \text{ V s}^{-1}$). (b) Cyclic voltammogram in the presence of 112 mM NaCN ($\nu = 0.2 \text{ V s}^{-1}$). (c) Cyclic voltammogram of isophthalonitrile (3.9 mM) in the presence of 660 mM NaCN ($\nu = 0.2 \text{ V s}^{-1}$). (d) Cyclic voltammogram of 3-chlorobenzonitrile (6.44 mM) in the presence of isophthalonitrile (3.9 mM) and NaCN 660 mM ($\nu = 0.2 \text{ V s}^{-1}$). (e) Variations of the height of the first two-electron irreversible peak with sweep rate and CN^- concentration. (f) Characteristic function of an ECE-substitution noncatalytic mechanism. Cyclic voltammograms of 2-chloroquinoline (0.6 mM) in liquid $\text{NH}_3 + 0.1 \text{ M NaI}$ at -40°C . Variations of the normalized peak height of the first wave, i_p/i_p^0 , with sweep rate (a) and ArX and CN^- concentrations (b). [ArX] = 0.6 (●), 1.8 mM (▲). The solid line (b) is the working curve for a disproportionation-substitution noncatalytic mechanism relating i_p/i_p^0 to the dimensionless parameter $\epsilon = k_D[\text{ArX}]/k_2[\text{CN}^-]$.

an ECE context; i.e., reaction 3 predominates over reaction 4 and reaction 5 over reaction 6 and 7. It follows that the dimerization of the isophthalonitrile anion radical should not interfere kinetically in the decrease of the first peak height which should then be controlled solely by the competition between reaction 3 and 5. The same theory as applied above in the case of 4-chloroquinoline and 4-chlorobenzonitrile is thus expected to be valid in the present case. This is indeed what was found as shown in Figure 5e,f. k_1/k_2 is thus found to be equal to $2.1 \times 10^{-2} \text{ M}$ and thus from the previously measured value of k_1 ($9.8 \times 10^5 \text{ s}^{-1}$)³⁸ k_2 is found as reported in Table I.

Qualitatively, the behavior exhibited by 2-chloroquinoline is similar. The decrease of the two-electron irreversible peak is, however, smaller, suggesting a less efficient coupling of the aryl radical with CN^- . On the other hand, even at high CN^- concentrations ($\sim 1 \text{ M}$) cycling over the 2-chloroquinoline wave does not produce any detectable $\text{ArCN}/\text{ArCN}^-$ wave in front of the ArX wave with sweep rates ranging from 0.1 to 100 V s^{-1} . This suggests that the dimerization of the anion radical of 2-cyanoquinoline is faster than that of isophthalonitrile and also that of 1-cyanonaphthalene (see below).¹⁴ The variations of the height of the two-electron irreversible peak of 2-chloroquinoline with the cyanide ion concentration, the substrate concentration, and the sweep rate are shown in Figure 6. It is noticed that the normalized peak height, i_p/i_p^0 , does not vary with the sweep rate and is an increasing function of the [ArX]/[CN⁻] concentrations ratio. Since the cleavage of the 2-chloroquinoline anion radical is slow ($k_1 = 1.7 \times 10^4 \text{ s}^{-1}$),^{5a,b} the electron transfer side reactions predominantly take place in the solution.¹⁵ This is confirmed by

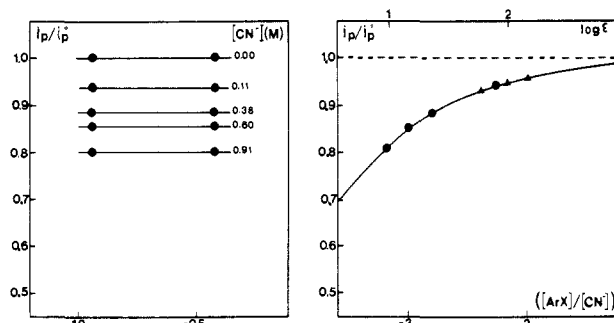


Figure 6. Cyclic voltammograms of 2-chloroquinoline (0.6 mM) in liquid $\text{NH}_3 + 0.1 \text{ M NaI}$ at -40°C . Variations of the normalized peak height of the first wave, i_p/i_p^0 , with sweep rate (a) and ArX and CN^- concentrations (b). [ArX] = 0.6 (●), 1.8 mM (▲). The solid line (b) is the working curve for a disproportionation-substitution noncatalytic mechanism relating i_p/i_p^0 to the dimensionless parameter $\epsilon = k_D[\text{ArX}]/k_2[\text{CN}^-]$.

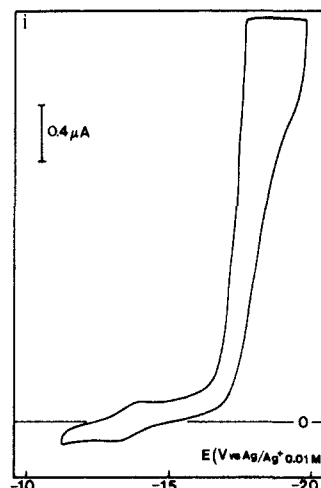
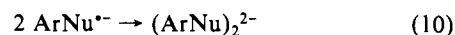


Figure 7. Cyclic voltammograms of 1-chloronaphthalene (3 mM) in liquid $\text{NH}_3 + 0.1 \text{ M KBr}$ at -40°C in the presence of 0.3 M NaCN, showing the appearance of the 1-naphthalonitrile wave upon cycling the 1-chloronaphthalene wave. Sweep rate, 0.2 V s^{-1} .

the fact that a plot of $\log [(2i_p - i_p^0)/(2i_p^0 - 2i_p)]$ vs. $\log [\text{CN}^-]$ differs quite significantly from the straight line with a $1/2$ slope characteristic of an ECE-substitution noncatalytic mechanism. The situation is thus similar to that found in the case of 4-bromobenzophenone. It is indeed observed that i_p/i_p^0 does not depend upon the sweep rate and varies with [ArX] and $[\text{CN}^-]$ in excellent agreement with the working curve, involving the competition parameter $\epsilon = k_D[\text{ArX}]/k_2[\text{Nu}^-]$, predicted for this type of mechanism^{3f} (Figure 6). Fitting the experimental points with the working curve and taking $k_D = 3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ leads to $k_2 = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. However, we have to consider the possible interference of the dimerization of the $\text{ArCN}^{\bullet-}$ radicals into the competition between the substitution process and the solution electron transfers to Ar^* . In contrast with the case of 3-chlorobenzonitrile where Ar^* is reduced at the electrode surface (ECE reaction scheme), owing to the fact that k_1 is now small and that reaction 4 functions from right to left ($E^\circ_{\text{ArCN}/\text{ArCN}^{\bullet-}} > E^\circ_{\text{ArX}/\text{ArX}^{\bullet-}}$), Ar^* is predominantly reduced by $\text{ArCN}^{\bullet-}$. Dimerization of the latter may thus well affect the competition between reactions 7 and 2. If the dimerization reaction



(15) The competition parameter between heterogeneous and homogeneous electron transfers, $(k_D[\text{ArX}]/k_1^{3/2})(Fv/RT)^{1/2}$, is between 20 and 40 in the sweep rate range 0.1–0.5 V s^{-1} , for [ArX] = 0.6 mM as used in the experiments reported in Figure 6. Competition is thus largely in favor of homogeneous electron transfer. This is further confirmed by previous observations made in the case of the reaction of the same substrate with thiophenoxide ions.^{5a,b} With this catalytic system the homogeneous electron transfer predominates, except at the highest extremity of the nucleophile concentration range.

(14) (a) The anion radical of the unsubstituted quinoline itself appears to undergo dimerization under similar conditions.^{14b} (b) Smith, W. H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 649.

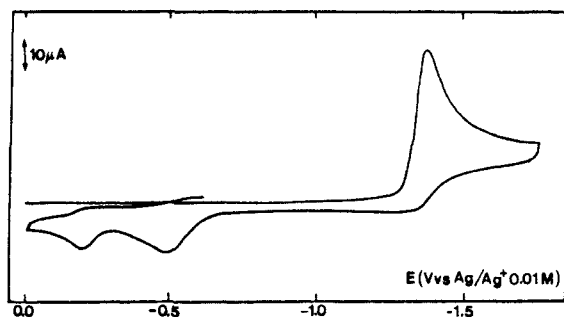
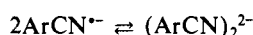
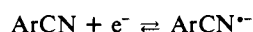


Figure 8. Cyclic voltammetry of 1-cyanonaphthalene (7.0 mM) in liquid $\text{NH}_3 + 0.1 \text{ M KBr}$ at -40°C . Sweep rate, 0.4 V s^{-1} .

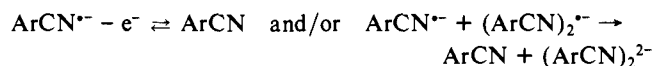
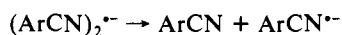
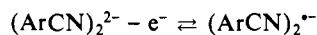
is very fast and if $(\text{ArNu})_2^{2-}$ is not able to reduce Ar^* , the latter radical will be predominantly reduced by ArX^* . This case has already been treated^{5b} and results in a significant variation of i_p/i_p^0 with the sweep rate, which is not observed here. We are thus led to conclude that either the dimerization reaction is not fast enough to alter significantly the competition between reaction 2 and 4 or that $(\text{ArNu})_2^{2-}$ is able to reduce Ar^* together with ArNu^* . In the latter case, the above derived value of k_2 would have been overestimated. This is the reason why we figured, in Table I, $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ as an upper limit of k_2 .

The 1-naphthyl radical is also not very reactive toward CN^- as shown by the fact that only a small decrease of the two-electron irreversible wave of 1-chloronaphthalene is observed upon addition of CN^- ions to the solution. i_p/i_p^0 goes to 0.95 and 0.925 in the presence of 0.15 and 0.30 M CN^- ions, respectively. However, a small reversible wave is visible at the foot of the 1-chloronaphthalene wave (Figure 7) corresponding to the 1-cyanonaphthalene redox couple as can be checked with an authentic sample. The cyclic voltammetry of the latter (Figure 7) shows that its anion radical dimerizes similarly to what happens with 9-cyanoanthracene in Me_2SO .¹⁶

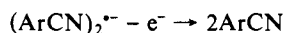


The dimer dianion thus formed is reoxidized in two steps upon scanning back the potential anodically, according presumably to the following mechanism:

first anodic wave



second anodic wave



The reversibility of the first cathodic wave of 1-cyanonaphthalene is a function of the sweep rate and the concentration. As expected, it increases with the first factor and decreases with the second. Treating the ratio of the anodic to the cathodic peak with the appropriate working curve¹⁷ allows the determination of the dimerization rate constant

$$k_{\text{dim}} = 10^3 \pm 200 \text{ M}^{-1} \text{ s}^{-1}$$

as an average of 12 determinations carried out for ArCN concentrations of 1.23, 2.30, 4.55, and 7.0 mM and sweep rates of 0.115, 0.200, and 0.380 V s^{-1} .

This is in agreement with the observation that the $\text{ArCN}/\text{ArCN}^{\bullet -}$ wave is reversible in the experiment where it was generated from the reaction of CN^- with the 1-naphthyl radical

(Figure 7). Under these conditions the average concentration of $\text{ArCN}^{\bullet -}$ radicals is indeed very small ($\sim 1.3 \times 10^{-4} \text{ M}$). Thus the kinetic parameter ($k_{\text{dim}}[\text{ArCN}^{\bullet -}]/v$)(RT/F) $\approx 1.3 \times 10^{-2}$ at 0.2 V s^{-1} , i.e., is small enough for dimerization to be ineffective within the time scale of the experiment.

The cleavage of the 1-chloronaphthalene anion radical is fast ($k_1 = 1.2 \times 10^7 \text{ s}^{-1}$).^{3h} The mechanism of the substitution reaction is thus of the ECE-substitution type as in the case of 4-chloroquinoline. From the (small) decrease of i_p observed upon addition of 0.15 and 0.30 M CN^- ions we obtained the value of k_2 reported in Table I.

For estimating the reactivity of the phenyl radical toward cyanide ions, we investigated first the reaction of chlorobenzene. The expected product, benzonitrile gives rise to a reversible reduction wave, its radical anion showing no tendency to dimerize even at low sweep rates. Upon addition of up to 0.3 M of CN^- to the solution, no significant decrease of the reduction wave of chlorobenzene is observed. Since the cleavage of chlorobenzene anion radical is fast ($4 \times 10^7 \text{ s}^{-1}$),^{3h} the reduction of Ph^* competing with the addition of CN^- is expected to occur predominantly at the electrode surface (reaction 5). We can therefore derive an estimation of the maximal value of k_2 , i.e., $k_2 \leq 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. It is possible to obtain a more precise estimation of the maximal value by using a substrate which anion radical cleaves more slowly than that of chlorobenzene. This is the case with diphenyl sulfide, the anion radical of which cleaves slowly ($k_1 = 10^4 \text{ s}^{-1}$).^{3h} The competition will then be with a solution electron transfer, namely, reaction 7, since we are under "necatalytic" conditions as in the case of 4-bromobenzophenone and 2-chloroquinoline. From the observation that the wave of diphenyl sulfide remains unaffected upon addition of up to 0.2 M CN^- ions, we thus conclude that $k_2 \leq 4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

Discussion

Comparison between the rate constants values listed in Table I and those previously obtained for the three nucleophiles PhS^- , $(\text{EtO})_2\text{PO}^-$, and $\text{CH}_3\text{COCH}_2^-$ ^{3b,h} shows that the cyanide ion is significantly less reactive. In the case of CN^- , the rate constants for all the aryl radicals we investigated are well below the diffusion limit ($3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) whereas for the three other nucleophiles they are close to the diffusion limit in most cases with the exception of the phenyl, the 2-quinolyl, and the 2-pyridyl radicals.^{3b,h}

The question, however, arises of whether this reflects a lower intrinsic reactivity of the cyanide ions or a larger extent of ion pairing with the sodium or potassium counterions in the case of CN^- . From the available data concerning the dissociation of NaCN , NaI , and KBr , it appears that the amount of free CN^- ions is quite small under our experimental conditions, about 5×10^{-3} of the total sodium cyanide introduced in the solution. Thus if we assume that only the free CN^- ions react, the k_2 values in Table I should be multiplied by a factor of 200. Ion pairing can also affect the reactivity of the other three nucleophiles but probably to a different extent in view of the change of the reacting center. The question of the effect of ion pairing of the anionic nucleophiles on their reactivity toward aryl radicals in liquid ammonia clearly deserves further investigations. This is presently under way on the basis of the attempt to use bulkier counterions or crown ethers complexing Na^+ or K^+ .

It is expected that an approximate correlation should exist between the rate constant k_2 and the standard potential of the $\text{ArNu}/\text{ArNu}^{\bullet -}$ couple in a series where the Ar moiety is varied and the nucleophile kept the same. On one hand

$$\Delta G_f^\ddagger = \Delta G^\circ_{\text{ArNu}^{\bullet -}} + \Delta G_c^\ddagger$$

with

$$\Delta G^\circ_{\text{ArNu}^{\bullet -}} = \Delta G^\circ_{\text{ArNu}} - FE^\circ_{\text{ArNu}/\text{ArNu}^{\bullet -}} + FE^\circ_{\text{Nu}^{\bullet -}/\text{Nu}^-}$$

(where $\Delta G^\circ_{\text{ArNu}^{\bullet -}}$ is the standard free energy of reaction 2, ΔG_f^\ddagger and ΔG_c^\ddagger are the activation free energies for the formation and cleavage of $\text{ArNu}^{\bullet -}$, respectively, $\Delta G^\circ_{\text{ArNu}}$ is the standard free energy of the Ar-Nu bond, and E° 's are the standard potentials of the subscript redox couples).

(16) Amatore, C.; Garreau, D.; Hammi, M.; Pinson, J.; Savéant, J. M. *J. Electroanal. Chem.* **1985**, *184*, 1.

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On the other hand, it has been shown, in the case of aryl halides, and rationalized on quantum chemical grounds that ΔG_c^\ddagger is roughly correlated with $E^\circ_{\text{ArNu}/\text{ArNu}^\bullet}$.¹⁸ Thus, when passing from one Ar^\bullet to the other

$$\Delta\Delta G_c^\ddagger \simeq \alpha F \Delta E^\circ_{\text{ArNu}/\text{ArNu}^\bullet}$$

should hold approximately. It follows that

$$\Delta\Delta G_f^\ddagger \simeq \Delta\Delta G^\circ_{\text{ArNu}} - (1 - \alpha) F \Delta E^\circ_{\text{ArNu}/\text{ArNu}^\bullet}$$

Since $\Delta G^\circ_{\text{ArNu}}$ is expected not to vary very much in the series, we end up with, as a rule of thumb, the more positive the standard potential of the $\text{ArNu}/\text{ArNu}^\bullet$ couple the faster reaction 2.

It is seen (Table I) that this rule is approximately obeyed in the present case. In particular, this explains why the phenyl radical exhibits the lowest reactivity in the series, as with the other nucleophiles.^{3b,h} Similarly, the low reactivity of the naphthyl radical is related to the fact that it is not activated by an electron-withdrawing group in contrast with the other members of the series. Two significant exceptions to the rule are the 2-quinolyl and the 2-cyanophenyl radicals. The low reactivity of the former, which was also noted with the other three nucleophiles,^{3g} can be ascribed to the electronic repulsion between the lone electrons pair of the adjacent nitrogen and the electrons of the C-Nu bond as discussed earlier.^{3g} The 2-cyanophenyl radical exhibits a remarkably high reactivity. We have no unequivocal explanation of this fact at present. One possibility is that the NaCN ion pair could par-

ticipate in the reaction, in this case, in contrast with the other aryl radicals, since transfer of the charge through the phenyl ring on the adjacent cyano group could help the dissociation of the ion pair in the transition state. This clearly calls for experimental verification in the context of a systematic study of the effect of ion pairing evoked earlier.

Experimental Section

The electrochemical instrumentation and the procedures for the work in liquid ammonia were the same as previously described.^{3g} The reference electrode was an Ag/Ag⁺ 0.01 M electrode. The working electrode was either a gold disk (0.5-mm diameter), a platinum disk (0.5-mm diameter), or a mercury drop hanged to a 0.5-mm diameter gold disk as indicated in Table I.

Registry No. Phenyl radical, 2396-01-2; 1-naphthyl radical, 2510-51-2; 2-cyanophenyl radical, 95936-64-4; 3-cyanophenyl radical, 95936-65-5; 4-cyanophenyl radical, 56263-67-3; 2-quinolyl radical, 54978-39-1; 4-benzoylphenyl radical, 59922-54-2; 4-quinolyl radical, 54978-41-5; chlorobenzene, 108-90-7; diphenyl sulfide, 139-66-2; 1-chloronaphthylene, 90-13-1; 2-chlorophenyl nitrile, 873-32-5; 3-chlorophenyl nitrile, 766-84-7; 4-bromophenyl nitrile, 623-00-7; 4-chlorophenyl nitrile, 623-03-0; 2-bromoquinoline, 2005-43-8; 4-benzoylphenyl bromide, 134-85-0; 4-bromoquinoline, 611-35-8; sodium cyanide, 143-33-9; cyanide ion, 57-12-5; benzonitrile, 100-47-0; 1-cyanonaphthalene, 86-53-3; 1,2-dicyanobenzene, 91-15-6; 1,3-dicyanobenzene, 626-17-5; 1,4-dicyanobenzene, 623-26-7; 2-cyanoquinoline, 1436-43-7; 4-benzoylbenzotrile, 1503-49-7; 4-cyanoquinoline, 2973-27-5; benzonitrile radical anion, 34478-18-7; 1-cyanonaphthalene radical anion, 34478-12-1; 1,2-dicyanobenzene radical anion, 34536-45-3; 1,3-dicyanobenzene radical anion, 34536-46-4; 1,4-dicyanobenzene radical anion, 34536-47-5; 2-cyanoquinoline radical anion, 75892-92-1; 4-benzoylbenzotrile radical anion, 60466-04-8; 4-cyanoquinoline radical anion, 68271-78-3.

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Structure and Reactivity of Thiophosphoranyl Radicals. A Quantum Chemical Study

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Abstract: Various optimized geometries were calculated for the $(\text{PH}_3\text{SH})^\bullet$ radical by using the unrestricted Hartree-Fock method with a 4-31G basis set and d polarization orbitals. The $(\text{PH}_3\text{SH-e})^\bullet$ form resembling a trigonal-bipyramidal structure with missing equatorial substituent (TBP-e) was the minimum energy structure. It appears that a σ^* arrangement is not stable but leads to dissociation. A potential surface for $\text{PH}_3 + \text{SH}^\bullet \rightarrow (\text{PH}_3\text{SH})^\bullet$ indicates a preferred attack where the incoming SH^\bullet enters an equatorial position. The pathways of dissociation into PH_3 and SH^\bullet are described, and the transition states are calculated. This approach was generalized with OH ligands: the results show identical behavior.

1. Introduction

The promoter role of phosphite in the photosynthesis of thiols by thiyyl radical trapping is a well-known experimental fact.¹ The interpretation of the mechanisms involved is controversial, especially since the results of both experimental and theoretical work for the last 15 years have led to contradictory conclusions concerning both the structure of the radicals and their possibilities of further reaction.

A trigonal-bipyramid structure with missing equatorial ligand (TBP-e) was initially proposed as being energetically favorable for these radicals. These conclusions were based on the values of ³¹P hyperfine isotropic couplings obtained with ESR in liquid

phase and on the results of several theoretical studies.²⁻⁶

The recent development of anisotropic ESR coupled with X-ray diffraction has generated results causing prior findings to be reconsidered. Thus, the possibility of structures different from

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