ether, 0.302 M in diethylamine, and 0.0312 M in 1,8-biphenylenediol.

Registry No. Diethylamine, 109-89-7; phenylglycidyl ether, 122-60-1; phenol, 108-95-2; *p*-chlorophenol, 106-48-9; *m*-chlorophenol, 108-43-0; *m*-nitrophenol, 554-84-7; *p*-cyanophenol, 767-00-0; *p*-nitrophenol, 100-02-7; catechol, 120-80-9; 1-biphenylenol, 1078-07-5; 8-methoxy-1-biphenylenol, 98945-48-3; 1,8-biphenylenediol, 18798-64-6; 1-(diethylamino)-3-phenoxy-2-propanol, 15288-08-1.

Kinetics of the Reaction of Alkylamines with 7,7,8,8-Tetracyanoquinodimethane (TCNQ) in Organic Solvents

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The following sequence of substitution reactions was studied spectrophotometrically in organic solvents:

$$\mathrm{RNH_2} + \mathrm{TCNQ} \xrightarrow{-\mathrm{HCN}} \text{7-substituted TCNQ} \xrightarrow[-\mathrm{HCN}]{+\mathrm{RNH_2}} \text{7,7-disubstituted TCNQ}$$

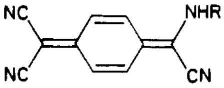
where R = butyl, octyl, dodecyl, and hexadecyl. The production of 7-(alkylamino)-7,7,8-tricyanoquinodimethanes proceeds via the formation of the anion radical of TCNQ ($\mathrm{TCNQ}^{-}\cdot$) whose rate of appearance was found to be a function of the chain length of R, reaching a maximum for octylamine. The formation of $\mathrm{TCNQ}^{-}\cdot$ was sensitive to the solvent polarity and electron-donor power and was associated with a small enthalpy and a highly negative entropy of activation. Above a certain [$C_8H_{17}NH_2$] the rate of disappearance of $\mathrm{TCNQ}^{-}\cdot$ was independent of the amine concentration, and the reaction had a much higher enthalpy and entropy of activation. The occurrence of tautomerism precluded an investigation of the conversion of 7-(octylamino)-7,8,8-tricyanoquinodimethane into 7,7-bis(octylamino)-8,8-dicyanoquinodimethane. A study of the reaction of octylamine with 7-morpholino-7,8,8-tricyanoquinodimethane (which does not exist in tautomeric forms) showed that the second substitution step proceeds with the same mechanism as the first one. The only difference between the two compounds (TCNQ and its monosubstituted morpholino derivative) is one of reactivity.

The strong Lewis acid 7,7,8,8-tetracyanoquinodimethane (TCNQ) forms a myriad of charge-transfer complexes and salts with very interesting properties[2-5] and undergoes substitution reactions[2,3,6] similar to nucleophilic vinylic substitutions.[7] Little attention has been given, however, to studying the kinetics and mechanism of formation of TCNQ derivatives.[3,8] The use of this dye to determine the critical micelle concentration of surfactants[10] is complicated due to the occurrence of side reactions, especially with alkylammonium carboxylates.[11] As a first step in investigating this micelle-mediated interaction we studied the kinetics of the reaction of alkylamines with TCNQ in organic solvents. Our results showed that the reaction rate was dependent on the amine structure and the solvent used.

Experimental Section

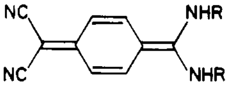
Melting points were not corrected. The spectrometers used were Zeiss DMR-21, PM6KS (UV–vis), Perkin-Elmer 238 (IR), Varian T-60, EM-360 (^{1}H NMR). The solvents, alkylamines, and TCNQ (Aldrich and Merck) were purified as given elsewhere.[12,13]

The reaction between TCNQ and an amine, e.g., RNH_2, can produce mono- (type I) and/or disubstituted derivative (type II) as depicted. The preparation of these derivatives for compounds with R = butyl, octyl, and dodecyl was given elsewhere,[11] those for R = hexadecyl were similarly prepared. The following results were obtained: the purple brown 7-(hexadecylamino)-7,8,8-tricyanoquinodimethane had a mp of 98–99 °C. Anal. Calcd for $C_{27}H_{38}N_4$: C, 77.47; H, 9.15; N, 13.38. Found: C, 77.41; H, 9.15; N, 13.48. IR (KBr) $\nu_{\mathrm{N-H}}$ 3225, $\nu_{\mathrm{C-H}}$ 3030, $\nu_{\mathrm{C\equiv N}}$ 2201, 2188, and $\nu_{\mathrm{C=C}}$ 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H), 1.34 (s, 28 H), 1.85 (m, 2 H), 4.00 (t, 1 H), 7.88 (q, 4 H). The yellow 7,7-bis(hexadecylamino)-8,8-dicyanoquinodimethane had a mp of 219–221 °C. Anal. Calcd for $C_{42}H_{72}N_4$: C, 79.68; H, 11.46; N, 8.85. Found: C, 79.52; H, 11.34; N, 8.74. IR (KBr) $\nu_{\mathrm{N-H}}$ 3192, 3104, $\nu_{\mathrm{C-H}}$ 3050, $\nu_{\mathrm{C\equiv N}}$ 2181, 2138, and $\nu_{\mathrm{C=C}}$ 1600 cm^{-1}; ^{1}H NMR



type I compound

7-(alkylamino)-7,7,8-tricyanoquinodimethane



type II compound

7,7-bis(alkylamino)-8,8-dicyanoquinodimethane

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[1] (a) Divisão, Tēcnica, Hoechst do Brasil, Suzano, S.P. (b) UNESP, Botucatu, S.P.

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[6] Hertler, W. R.; Hartzler, H. D.; Acker, D. S.; Benson, R. E. *J. Am. Chem. Soc.* **1962**, *84*, 3387.

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[8] Most TCNQ-related kinetic work has been focused on electron-transfer reactions to produce its highly stabilized green anion radical ($\mathrm{TCNQ}^{-}\cdot$). For some examples, see ref 2 and 9.

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[12] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals", 2nd ed.; Pergamon Press: New York, 1980.

[13] Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370.

0022-3263/85/1950-5099$01.50/0

($CDCl_3$) δ 0.88 (t, 6 H), 1.29 (s, 56 H) 1.73 (m, 4 H), 3.51 (t, 2 H), 7.08 (q, 4 H).

The compound 7-morpholino-7,8,8-tricyanoquinodimethane was prepared by stirring 2.8 mmol of morpholine and 2.5 mmol of TCNQ in 50 mL of THF under nitrogen, at room temperature for 12 h. The solvent was evaporated and the residue purified by column chromatography (silica gel, 3:1 acetone–hexane). The deep blue fraction was collected, the solvent evaporated, and the product submitted to analyses. The solid did not melt up to 230 °C (dec).[14] Anal. Calcd for $C_{15}H_{12}N_4O$: C, 68.17; H, 4.58, N, 21.20. Found: C, 68.84; H, 4.86; N, 20.91; ^1H NMR (Me_2SO-d_6) δ 3.45 (m, 4 H), 3.97 (m, 4 H), 7.89 (q, 4 H). In acetonitrile the compound had absorption maxima at 620 and 646 nm and reacted with morpholine, producing 7,7-dimorpholino-8,8-dicyanoquinodimethane as the only product (λ_{max} = 418 nm) with an isosbestic point at 474 nm.

The corresponding type II compound was prepared as given elsewhere[6] and crystallized from ethanol: mp 340–345 °C.[14] Anal. Calcd for $C_{18}H_{20}N_4O_2$: C, 66.64; H, 6.22; N, 17.27. Found: C, 66.49; H, 6.14; N, 17.45; ^1H NMR (Me_2SO-d_6) δ 3.55 (m, 8 H), 3.82 (m, 8 H), 7.18 (q, 4 H). In CH_3CN the yellow compound absorbs at λ_{max} = 418 nm.

The ion radical pair ($C_8H_{17}NH_2^{+}\cdot$)·$TCNQ^{-}\cdot$ which was used in the kinetic studies (vide infra) was prepared and purified as follows. A small aliquot (0.4 mL) of a 0.5 M octylamine solution in petroleum ether was added to a cold solution of TCNQ (0.001 M) in dichloromethane–petroleum ether (20%, v/v) and the mixture kept at 0 °C for 10 min. The bluish green precipitate was filtered and washed with cold dichloromethane until the filtrate was free from TCNQ (checked in the visible region). It was then dissolved in the minimum amount of cold acetonitrile and used immediately.

Reaction kinetics were carried out under pseudo-first-order conditions (amine in excess). Since dissolved oxygen can affect the results[16] the solvents were N_2 saturated; all glassware and reaction cuvettes were flushed with N_2. The reaction of TCNQ was followed at 390 nm, that of the ion radical pair at 745 nm, and that of 7-morpholino-7,8,8-tricyanoquinodimethane at 646 nm. All runs (carried out at least in duplicate) exhibited first-order kinetics over more than three half-lives and observed rate constants (k_{obsd}) were reproducible to ±2%.

Results and Discussion

Because of the multistep nature of the reaction under consideration some of its features will be discussed before analyzing the kinetic data. Addition of an alkylamine to a TCNQ solution results in the instantaneous production of an intense green color, which then changes to purple-brown. In the presence of excess amine the solution turns yellow. These changes can be represented by eq 1. The

$$RNH_2 + TCNQ \rightarrow (RNH_2^{+}\cdot)\cdot TCNQ^{-}\cdot \xrightarrow{-HCN} \text{type I compound (purple-brown)} \xrightarrow[-HCN]{+RNH_2} \text{type II compound (yellow)} \quad (1)$$

formation of a charge-transfer complex between the amine and TCNQ most certainly precedes the electron transfer step which leads to the production of $TCNQ^{-}\cdot$. Attempts to detect the formation of this complex by monitoring the spectra in the visible region were unsuccessful due to the intense absorption of the anion radical (peaks at 420, 685, 749, 768, and 842 nm). Whereas the detection of the charge-transfer complexes between tertiary aromatic amines and TCNQ is relatively simple,[3,9,17] the same is not true for primary and secondary amines.[18] These complexes are, however, accepted as the first intermediates in the substitution reactions of TCNQ[3] and those of the structurally similar tetracyanoethylene (TCNE).[2,7,19]

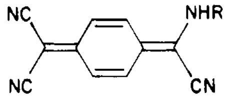
Table I. Effect of the Chain Length of the Alkylamine (RNH_2) and of the Solvent on the Rate Constants of the Forward (k_1) and Reverse (k_{-1}) Reactions at 25 °C

R	k_1[b]	k_{-1}[b]
effect of R[a]		
butyl	48.52	0.036
octyl	63.22	0.023
dodecyl	43.77	0.019
hexadecyl	40.29	0.011

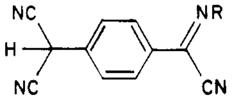
solvent	k_1[b]	k_{-1}[b]
effect of the solvent[c]		
benzene	50.21	0.053
chloroform	9.89	0.024
dichloroethane	167.13	0.157
dichloromethane	63.22	0.023
tetrachloroethylene	42.56	0.054

[a] In dichloromethane. [b] Units are $M^{-2}\ s^{-1}$ for k_1 and $M^{-1}\ s^{-1}$ for k_{-1}. Errors in k_1 are ≤2.5%. [c] For the reaction of TCNQ with octylamine.

The conversion of the ion radicals into monosubstituted TCNQ derivatives is accompanied by sharp isosbestic points (e.g., at λ = 662 nm, R = butyl, CH_2Cl_2).[11] This lends credence to the suggestion that this step proceeds via the intermediate formation of $(CN)_2CHC_6H_4$-p-C$(CN)_2NHR$ which then loses HCN rapidly to give product I.[3,20] The latter is capable of existing in the tautomeric forms Ia and Ib, and we found that the equilibrium lies in favor of Ia in less polar solvents.[22] Type II compounds usually exist in the quinonoid form.[3,6]



Ia-(purple)



Ib-(brown)

We have studied the kinetics of the formation and decomposition of the ion radical pair. Many studies of TCNQ[3,8,17] and of TCNE[16] showed that the formation of the ion radicals from the parent charge-transfer complexes is reversible. Our kinetic data (Table I-A, supplementary material) fit eq 2, where k_{obsd} is that given before and k_1

$$k_{obsd} = k_1[RNH_2]^2 + k_{-1}[RNH_2] \quad (2)$$

and k_{-1} are the rate constants for the forward and reverse reaction, respectively. A plot of $k_{obsd}/[RNH_2]$ vs. $[RNH_2]$ is linear as required by eq 2 (Figure 1, supplementary material), and the dependence of the individual rate constants on the chain length of the alkyl group of the amine is given in Table I. The dependence of the values of k_{obsd} on the solvent used is shown in Table I-B (supplementary material), and the corresponding values of k_1 and k_{-1} are given in Table I.

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[14] Many TCNQ-based compounds decompose before melting or exhibit a very broad melting range.[3,6,15]

[15] Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1962**, *84*, 3374.

[16] Farrell, P. G.; Ngô, P. N. *J. Chem. Soc., Perkin Trans. 2* **1974**, 552.

[17] Poradowska, H.; Nowak, K. *Bull. Soc. Chim. Fr.* **1977**, 535. Poradowska, H.; Czuba, W. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 42.

[18] Garnovskii, A. D.; Utkina, L. S.; Sheinker, V. N.; Osipov, O. A.; Zaletov, V. G. *Zh. Obsch. Khim.* **1974**, *44*, 2246. Bhat, S. N. *Indian J. Chem., Sect. A* **1976**, *14A*, 791.

[19] Rappoport, Z. *J. Chem. Soc.* **1963**, 860. Rappoport, Z.; Greenzaid, P.; Horowitz, A. *Ibid.* **1964**, 1334. Rappopport, Z.; Horowitz, A. *Ibid.* **1964**, 1348.

[20] That is, the formation of this intermediate is rate limiting.[21] A simple route is by association of the oppositely charged ion radicals to give the zwitterion $(CN)_2^{-}C_6H_4$-p-C$(CN)_2N^{+}H_2R$ followed by fast proton transfer.

[21] Isaacs, N. S. "Reactive Intermediates in Organic Chemistry"; Wiley: London, 1974.

[22] The visible spectrum of the compound with R = butyl in CH_2Cl_2–hexane shows this equilibrium shift. Thus the intensity of the peak at 420 nm (due to Ib)[3] decreased as a function of decreasing the concentration of CH_2Cl_2 in the solvent.

The second-order dependence on $[RNH_2]$ in eq 2 suggests that the reaction pathway involves either a general base-catalyzed amine attack[23] or an (kinetically indistinguishable) attack by amine dimers. Published work on the association of aliphatic amines in organic solvents showed, however, no detectable association in the amine concentration range used in the present study.[25]

Due to the small values of k_{-1}, no quantitative significance will be placed on its variation as a function of the amine chain length. Table I. shows, however, that k_1 increases in going from butyl- to octylamine and then decreases for dodecyl- and hexadecylamine. It is interesting that this same dependence on the chain length has also been observed for ester aminolysis by alkylamines in benzene and for the association of several substrates with a series of alkylammonium propionates in carbon tetrachloride.[26] This dependence is probably due to small differences in pK_a values and increasing steric hinderance along the amine series.[27] In water, at 25 °C, the pK_a of butyl-, octyl-, dodecyl-, and hexadecylamine are 10.61, 10.65, 10.63, and 10.61, respectively.[29] In the aprotic solvents used the difference between the individual pK_a values is probably bigger due to the absence of the solvent leveling effect. Additionally, it appears that the steric effect due to chain coiling[30] is not appreciable for octylamine so that it is showing the highest reactivity.

Having established that octylamine is most reactive we proceeded to study the effect of the solvent on the reaction rate. Table I shows, not unexpectedly, that the reaction is very sensitive to the nature of the solvent. Thus changing the latter from dichloromethane to dichloroethane, which is only slightly more polar,[31] resulted in a threefold increase in the value of k_1. an excellent linear correlation was found between $\log k_1$ and E_T, the solvent empirical polarity parameter,[31] for the saturated solvents (correlation coefficient = 0.998). No such correlation existed, however, when the points for benzene and tetrachloroethylene were included (correlation coefficient = 0.255) because the reactions in these solvents were much faster than expected based only on their E_T values. In a detailed analysis of the effect of solvents on physical and chemical properties it has been shown that linear correlations between spectroscopic, rate, and equilibrium data and a single solvent property are not very common. Combination of E_T with another solvent property usually leads to a better correlation.[32] This idea was tested as in eq 3, where a and b are regression coefficients and C is

$$\log k_1 = aE_T + bC \qquad (3)$$

another solvent property that was applied to the data of Table I, substituting the solvent-dependent functions analyzed in ref 32 for C.[33] The quality of the fit to the equation was judged by comparing the sums of the squares of the residues ($\sum Q^2$)[34] obtained for each different C. A much better fit ($\sum Q^2 = 0.120$ compared to values between 0.516 and 0.746 for the other functions) was obtained when C represented the electron-donor power of the solvent.[35]

Activation parameters for the formation of the ion radical pair were determined from a study at different temperatures (octylamine, CH_2Cl_2). The reaction was found to be associated with $\Delta H^{\ddagger} = 4.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -34.5$ eu.[37] This small enthalpy of activation is interesting since the reaction is not fast. There are many reactions, however, that are known to occur at normal rates and that have small $\Delta H^{\ddagger}$ or even display negative temperature coefficients (i.e., $\Delta H^{\ddagger} < 0$).[38] One explanation that fits the present case is that an equilibrium (e.g., formation of a charge-transfer complex) precedes the reaction step that is being followed, so that the calculated enthalpy is, in fact, the sum of the enthalpies of the two steps.[38] Available data show that the formation of TCNQ-based charge-transfer complexes is exothermic ($\Delta H^{\circ} \sim -2$ to -4 kcal mol^{-1}),[18] implying that $\Delta H^{\ddagger} > 7$ kcal mol^{-1}. The second-order dependence on the amine concentration (eq 2) is clearly reflected in the highly negative value of $\Delta S^{\ddagger}$.

We have also studied the transformation of the ion radical pair into 7-(octylamino)-7,8,8-tricyanoquinodimethane as a function of $[C_8H_{17}NH_2]$ in dichloromethane. The reaction rate was found to increase as a function of increasing the amine concentration, reaching a constant value when $[C_8H_{17}NH_2] \geq$ ion radical pair. It appears that the second amine molecule of the ion radical pair[23] was washed out during its purification (vide Experimental Section). Once this molecule is replaced the reaction becomes independent of the amine concentration; i.e., it becomes first order in $[(C_8H_{17}NH_2{}^{+}\cdot)\cdot TCNQ^{-}\cdot]$, similar to the case of TCNE.[16] The activation parameters were determined in the presence of excess amine and were $\Delta H^{\ddagger} = 13.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -30.8$ eu.[39] That is, the decomposition reaction is accompanied by higher enthalpy and entropy of activation (compared to the formation of $TCNQ^{-}\cdot$). This is not surprising in view of the high energy and little reorganization expectedly required to reach the precursor of the TCNQ monosubstituted product, i.e., the intermediate $(CN)_2CHC_6H_4C(CN)_2NHC_8H_{17}$.[3,20]

We attempted to study the kinetics of the conversion of 7-(octylamino)-7,8,8-tricyanoquinodimethane into 7,7-bis(octylamino)-8,8-dicyanoquinodimethane in dichloromethane. When type I compound was treated with octylamine the pinkish solution instantaneously turned yellow, and a single peak at 422 nm (432 nm in acetonitrile) appeared whose intensity was independent of the time or $[C_8H_{17}NH_2]$. The same type of behavior was observed if

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(23) For example, to give the species $[(RH_2N\cdots H_2NR)^{+}\cdot]\cdot TCNQ^{-}\cdot$ similar to that suggested for the reaction of anilines with TCNE in the same solvent.[24]

(24) Farrell, P. G.; Ngô, P. N. *J. Chem. Soc., Perkin Trans 2* **1973**, 974.

(25) Fenney, J.; Sutcliffe, L. H. *J. Chem. Soc.* **1962**, 1123. Höpfner, A.; Höpfner, H. M. *Ber. Bunsenges. Phys. Chem.* **1964**, *68*, 410.

(26) El Seoud, O. A.; Pivêtta, F.; El Seoud, M. I.; Farah, J. P. S.; Martins, A. *J. Org. Chem.* **1979**, *44*, 4832. El Seoud, O. A.; Ribeiro, F. P. *Ibid.* **1976**, *41*, 1365.

(27) Differences in basicity and steric effects have been used to explain the results of interaction of TCNQ with a series of *N*-alkyl-*p*-phenylenediamines.[28]

(28) Ohmasa, M.; Kinoshita, M.; Sano, M.; Akamatu, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1998.

(29) Hoer, C. W.; McCorkle, M. R.; Ralston, A. W. *J. Am. Chem. Soc.* **1943**, *65*, 328.

(30) Murakami, Y.; Aoyama, Y.; Kida, M. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1974.

(31) Reichardt, C. "Solvent Effects in Organic Chemistry"; Verlag Chemie: Weinheim, 1979.

(32) Fowler, F. W.; Katritzky, A. R.; Rutherford, R. J. D. *J. Chem. Soc. B* **1970**, 460.

(33) These functions are based on the following solvent properties: dielectric constant, index of refraction, solvent-induced spectral shifts.[32]

(34) A residue is the difference between the values of an experimental and a calculated data point.

(35) A convenient measure for this property is that based on the difference between the stretching frequency (ν_{O-D}) of methanol-*d* in the solvent in question and that in benzene.[36]

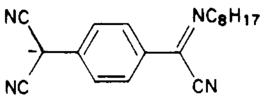
(36) Kagiya, T.; Sumida, Y.; Inoue, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 767.

(37) Based on k_1 values of 38.97, 45.06, 58.18, 63.22, and 68.67 M^{-2} s^{-1} for the reaction at 9.4, 15.1, 22.0, 25.0, and 28.0 °C, respectively. The error in $\Delta H^{\ddagger}$ is 0.3 kcal mol^{-1} and in $\Delta S^{\ddagger}$ is 1 eu.

(38) Leenson, I. A.; Sergeev, G. B. *Russ. Chem. Rev. (Engl. Transl.)* **1984**, *53*, 417 and references cited therein.

(39) Based on k_{obsd} values of (0.60, 0.94, 1.42, and 2.09) × 10^{-4} s^{-1} for the reaction at 10, 15, 20, and 25 °C, respectively, in the presence of 0.007 M octylamine. The error in $\Delta H^{\ddagger}$ is 0.2 kcal mol^{-1} and in $\Delta S^{\ddagger}$ is 0.5 eu.

the TCNQ monosubstituted derivative was treated with other bases including butylamine, *N*,*N*-dimethyloctylamine, pyridine, and sodium hydroxide (the latter in acetonitrile). Since 7-(alkylamino)-7,8,8-tricyanoquinodimethanes are soluble in alkaline solutions from which they can be precipitated on acidification,[6,11] it is clear that what is being observed is simply the deprotonation of tautomer Ib to give the anion



which is not susceptible to nucleophilic attack.

A type I compound obtained from the reaction of TCNQ with a secondary amine cannot, however, exist in tautomeric forms, rendering a study of the required transformation feasible. Indeed, the deep blue 7-morpholino-7,8,8-tricyanoquinodimethane reacts smoothly with morpholine, producing the TCNQ 7,7-dimorpholino derivative as the only product (see Experimental Section). It also reacts with octylamine to give 7-morpholino-7-(octylamino)-8,8-dicyanoquinodimethane with a sharp isosbestic point at 475 nm (CH_3CN). That is, the reaction under consideration either occurs in one step or via an intermediate whose formation is rate limiting.[21] In view of what is known about the chemistry of substitution reactions of TCNQ[3,6] and TCNE[2,7,19] the second route is the plausible one.

The reaction of octylamine with 7-morpholino-7,8,8-tricyanoquinodimethane showed features similar to those observed for the octylamine–TCNQ reaction, except for lower rates. Thus whereas the latter reaction is very fast in acetonitrile, the former can be conveniently studied in this solvent, where it was found to be sluggish in dichloromethane. This is understandable in terms of the differences in reactivity (as Lewis acids) between the parent dye and its monosubstituted derivative, most probably coupled with some steric hiderance due to the substitution of the morpholine ring for the CN group. A kinetic study in acetonitrile yielded rate constant expression similar to eq 2 with $k_1 = 1.58\ M^{-2}\ s^{-1}$ and $k_{-1} = 0.0037\ M^{-1}\ s^{-1}$. Due to the intense absorption of the reactant and of the product, attempts to detect the formation of a charge-transfer complex were not sucessful; however, its exothermic formation accounts for the very small ΔH^* obtained, 1.4 kcal mol^{-1}.[40] The participation of a second amine molecule as a general base catalyst can be used to explain the highly negative ΔS^* value, −53 eu.[40] In summary, it seems that the second substitution reaction proceeds via the same mechanism suggested for substitution of the first CN group, the only differences is one of reactivity.

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Supplementary Material Available: Tables of observed rate constants of reaction of RNH_2 with TCNQ and dependence of k_{obsd} for reaction of octylamine and figure of $k_{obsd}/[RNH_2]$ vs. $[RNH_2]$ (4 pages). Ordering information is given on any current masthead page.

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[40] Calculated from the following k_{obsd} values obtained in the presence of 0.08 M octylamine: (7.9, 9.0, 10.1, and 10.6) × 10^{-3} s^{-1} at 15.1, 25.1, 35.7 and 40.4 °C, respectively. Since k_{-1} was negligible the values of k_1 were obtained from $k_1 = k_{obsd}/[C_8H_{17}NH_2]^2$. The error in ΔH^* is 0.2 kcal mol^{-1} and in ΔS^* is 0.5 eu.

Hydrogen Exchange between Methyl Viologen Cation and Basic Deuterium Oxide

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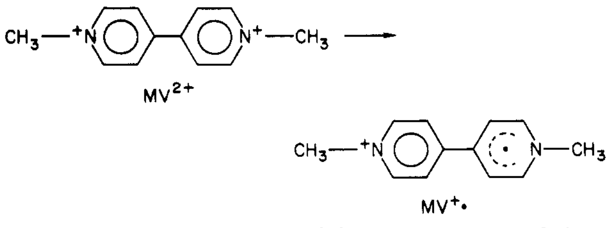
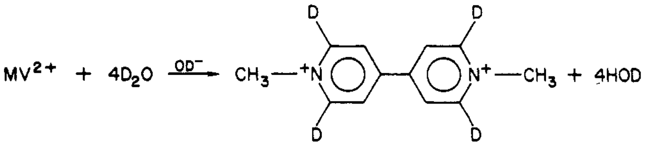
The methyl viologen cation has been found to exchange the 2,2′,6,6′-hydrogens with D_2O in basic solution. The rate, which can be conveniently followed by proton NMR at room temperature, is first order in both cation and hydroxide ion. The second-order rate constant at 24 °C and $\mu = 0.58$ is $1.7 \times 10^{-2}\ M^{-1}\ s^{-1}$. Activation parameters ΔH^* and ΔS^* have been found to be 80 kJ mol^{-1} and −8 J mol^{-1} K^{-1}, respectively. Benzyl viologen and diquat also exchange; however, multiple sites are involved so detailed studies have not been carried out.

The dipyridinium cation methyl viologen (MV^{2+}) is important as an electron-transfer reagent, and as the chloride salt (paraquat) it is used as a herbicide. The cation is known to undergo reduction in basic aqueous solution to give the radical–cation $MV^{+\cdot}$, eq 1). While investigating this reduction in alkaline D_2O by NMR, we found that the aromatic proton intensity of MV^{2+} decreased with time.



(1)

This was traced to exchange of the 2,6-set of hydrogens with D_2O (used as both solvent and NMR lock)–see eq 2; note that the numbering system used has the nitrogens at the 1- and 1′-positions on the ring.



(2)

Line-broadening of the proton NMR lines of MV^{2+} occurs when trace quantities of $MV^{+\cdot}$ are present.[1] Because

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[1] Johnson, C. S. *J. Chem. Phys.* **1963**, *39*, 2111.