# KINETICS OF ADDITION OF TETRACYANOETHYLENE TO ANTHRACENE AND BICYCLO[2,2,1]HEPTADIENE

P. BROWN and R. C. COOKSON

The University, Southampton

**Abstract**—The enthalpy of activation for Diels-Alder addition of tetracyanoethylene to anthracene ranges from only 4·2(5) Kcal mole$^{-1}$ in chloroform to 12·3 Kcal mole$^{-1}$ in *o*-xylene. In the aromatic solvents $\Delta H^{\ddagger}$ for addition to bicycloheptadiene is consistently 5–6 Kcal mole$^{-1}$ higher, and the rates for the two reactions respond to change in solvent in exactly the same way. An important factor seems to be the extent of incapacitation of tetracyanoethylene by $\pi$-complexing with the solvent, so the log of the second order rate constants varies linearly with $(K_e + 1)^{-1}$, the solvents with the largest $K_e$ (equilibrium constant for $\pi$-complex formation with tetracyanoethylene) giving the slowest reaction. In these solvents the solubility of tetracyanoethylene is directly proportional to $K_e$.

THE vast amount of work on the orientation, stereochemistry and synthetic application of the Diels-Alder reaction[1-3] has been supplemented by thorough investigation of its kinetics.[4-10] More recently, the reaction has been extended to the addition of dienophiles to classically unconjugated dienes, in which the two double bonds are held together other than by being directly joined by a single bond, namely bicyclo[2,2,1]heptadiene,[11,12] bicyclo[2,2,2]octadiene[13] and 1,3,5,7-tetramethylene-cyclooctane.[14] Trends of reactivity with various dienophiles suggested that bicyclohepta-diene behaves like its classically conjugated counterparts, e.g. cyclopentadiene, and it was shown that it has a greater preference for *endo*-addition than does cyclopenta-diene.[12] To relate the two reactions more exactly, the kinetics of addition[15] have now

[1] K. Alder, *Newer Methods of Preparative Organic Chemistry* p. 381. Interscience, New York (1948); K. Alder and M. Schumacher, *Prog. Chem. Org. Nat. Prod.* **10**, 1 (1953); K. Alder, *Experientia Suppl. II* 86 (1955).

[2] R. B. Woodward and T. J. Katz, *Tetrahedron* **5**, 70 (1959).

[3] Y. A. Titov, *Russ. Chem. Rev.* (English Trans.) 267 (1962).

[4] Reviewed up to then by C. K. Ingold, *Structure and Mechanism in Organic Chemistry* p. 711, Bell, London (1953).

[5] W. Rubin and A. Wassermann, *J. Chem. Soc.* 2205 (1950) and earlier papers.

[6] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.* **77**, 6284 (1955).

[7] J. A. Berson and A. Remanick, *J. Amer. Chem. Soc.* **83**, 4947 (1961); J. A. Berson, Z. Hamlet and W. A. Mueller, *Ibid.* **84**, 297 (1962).

[8] C. Walling and D. D. Tanner, *J. Amer. Chem. Soc.* **85**, 607 (1963).

[9] J. Sauer, H. Wiest and A. Mielert, *Chem. Ber.* **97**, 3183 (1964); J. Sauer, D. Lang and H. Wiest, p. 3209.

[10] K. E. Lewis and H. Steiner, *J. Chem. Soc.* 3080 (1964).

[11] E. F. Ullman, *Chem. & Ind.* 1173 (1958); A. T. Blomquist and Y. C. Meinwald, *J. Amer. Chem. Soc.* **81**, 667 (1959); H. K. Hall, *J. Org. Chem.* **25**, 42 (1960); T. L. Cairns, C. G. Krespan and B. C. McKusick, *J. Amer. Chem. Soc.* **83**, 3428 (1961); R. C. Cookson, S. S. H. Gilani and I. D. R. Stevens, *Tetrahedron Letters* 615 (1962); R. C. Cookson and J. D. Dance, *Ibid.* 879 (1962); S. J. Cristol, E. L. Allred and D. L. Wetzel, *J. Org. Chem.* **27**, 4058 (1962); C. D. Weis, *J. Org. Chem.* **28**, 74 (1963).

[12] R. C. Cookson, J. D. Dance and J. Hudec, *J. Chem. Soc.* 5416 (1964).

[13] R. O. Williams, Ph.D. Thesis, Southampton (1962).

[14] J. K. Williams and R. E. Benson, *J. Amer. Chem. Soc.* **84**, 1257 (1962).

[15] P. Brown and R. C. Cookson, *Abstract Papers, 148th A.C.S. Meeting* p. 7U. Chicago, Sept (1964)

been measured of a conjugated (anthracene = A) and an unconjugated diene (bicyclo-heptadiene = B) with the same dienophile (tetracyanoethylene = TCNE). The reaction of a diene of low ionization potential[16] with a dienophile of high electron-affinity[17] should also provide a system in which—if ever—a dipolar or diradical intermediate might be detected if it is present.
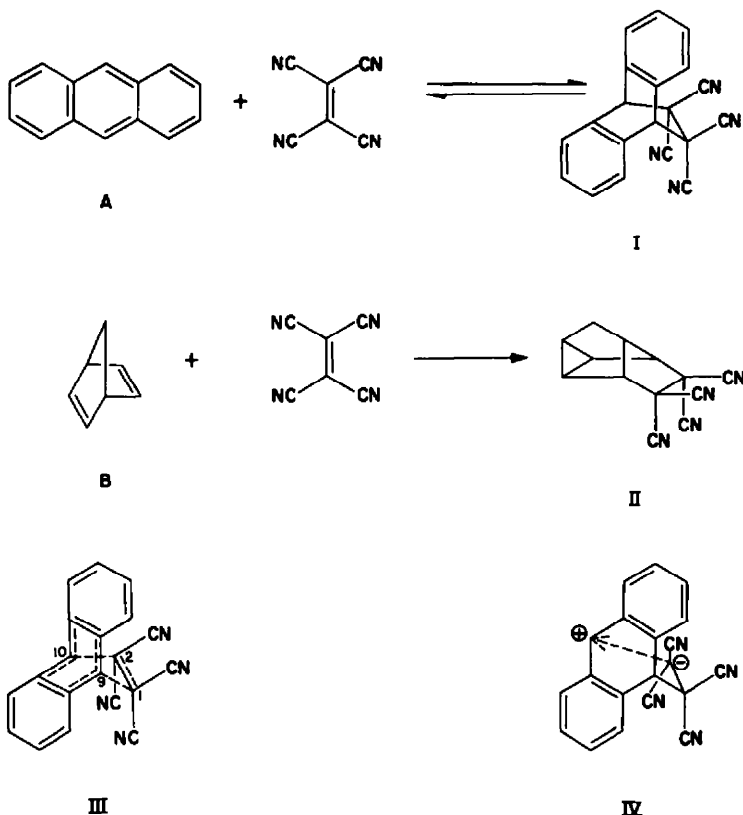


Tables 1 and 2 summarize the second order rate constants for addition of A to TCNE in a range of solvents and the resulting enthalpies and entropies of activation. At the temperatures used A reacts fastest with TCNE in chloroform, 1,2-dichloro-ethane and o-dichlorobenzene, the least basic solvents. The very low $\Delta H^{\ddagger}$ for chloro-form (4·25) can be compared with Andrews and Keefer's[6] value of 13·1 Kcal mole$^{-1}$ for addition of A to maleic anhydride in chloroform (determined at much higher concentrations of dienophile), and the $\Delta H^{\ddagger}$ of 11·0 in toluene compares with the reported activation energy of 19·5 Kcal mole$^{-1}$ for the reaction with acrylonitrile in the same solvent.[18] TCNE reacts about 10$^4$ times more slowly with B than with A,

[16] Anthracene:—a A. Streitwieser, J. Amer. Chem. Soc. 82, 4123 (1960);
                                    b M. Chowdhury, Trans. Faraday Soc. 57, 1482 (1961);
      Bicycloheptadiene:—S. Meyerson, J. D. McCollum and P. N. Rylander, J. Amer. Chem. Soc. 83, 1401 (1961).
[17] M. E. Peover, Trans. Faraday Soc. 58, 2370 (1962).
[18] M. Gillois and P. Rumpf, C.R. Acad. Sci. Paris 243, 853 (1956).

almost entirely due to a higher $\Delta H^{\ddagger}$ (averaging 5–6 Kcal mole$^{-1}$ for a common solvent). The large negative $\Delta S^{\ddagger}$ is identical for the two dienes and typical of cyclic reactions, the Diels-Alder reaction in particular.[4–10]

The A-TCNE kinetics provide ample data for an isokinetic plot of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$. A remarkably linear relationship exists, as has been found for a smaller range of solvents in the addition of $p$-benzoquinone to cyclopentadiene.[19] The slope corresponds to an absolute temperature of 298°, very near the mean experimental temperature, implying that $\Delta F$ for the reaction in all solvents is approximately constant, and that the linearity of the plot may be mainly due to experimental error, as well as to regular changes in solvation.[20] The more sensitive plot of log $k$/T against 1/T shows no isokinetic temperature (although in such a plot for B the lines for three out of six solvents do intersect at 395–405°).

In the solvents listed in Tables 1 and 2 at normal temperatures the equilibrium lies far over to the adduct. In alcohols (whether primary, secondary or tertiary) and in dioxan, however, it lies on the side of the addends for A-TCNE, probably mainly because of the greater $\pi$-basicity and complexing or reaction of these solvents with free TCNE. (For the same reason, reversibility of the reaction was observed in the kinetics at lower temperatures in $o$-xylene and toluene than in benzene.) Table 3 lists the rate constants for dissociation of the adduct in three such solvents. The remarkably close agreement of the rates and Arrhenius parameters for ethanol and dioxan show that hydrogen-bonding in the transition state is unimportant, and that the irreversible solvolysis of the liberated TCNE by alcohols does not affect the rate.

No dissociation of the B-TCNE adduct could be detected after 48 hr at 50° in ethanol or dioxan.

The parallel response of the rate of addition of A and B to TCNE to change in solvent is strikingly shown by plotting the rate constant for addition of A in the range of aromatic solvents from Table 1 relative to the rate in benzene against the rate for B in the same solvents relative to its rate in benzene (Fig. 1). *The points lie on a straight line of unit slope.*

Except for a broad trend for more polar solvents to increase the rate of reaction. there is little correlation of rate with macroscopic dielectric constant, $D^{-1}$ or $(D-1) \times (2D+1)^{-1}$ (Table 1). In aromatic solvents the rates for A or B roughly follow the $\sigma_m$ value of the substituent on the benzene ring of the solvent molecule (e.g. Fig. 2): $\sigma_p$ achieves a significantly poorer correlation. This suggests that the inductive influence of the substituent is affecting the $\pi$-basicity of the aromatic solvent, and changing the rate largely by the more basic solvents buffering the solution and reducing the concentration of free, uncomplexed TCNE. The suspicion that this may be an important factor is borne out by the regular increase in $\Delta H^{\ddagger}$ with $K_0$ for aromatic solvents, the equilibrium constant for 1:1 $\pi$-complex formation with TCNE[21] (measured in methylene dichloride solution). The only notable exception is anisole, which produces a lower $\Delta H^{\ddagger}$ and faster rate than expected from its $K_0$.

[19] R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.* 538 (1937); A. Wassermann, *Ibid.* 623 (1942).

[20] J. E. Leffler, *J. Org. Chem.* **20**, 1202 (1955); R. F. Brown, *Ibid.* **27**, 3015 (1962); J. E. Leffler and E. Grunwald, *Rates and Equilibria of Organic Reactions* pp. 315–402. J. Wiley, New York (1963); R. C. Petersen, *J. Org. Chem.* **29**, 3133 (1964); O. Exner, *Coll. Czech. Chem. Comm.* **29**, 1094 (1964).

[21] R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.* **80**, 2778 (1958).
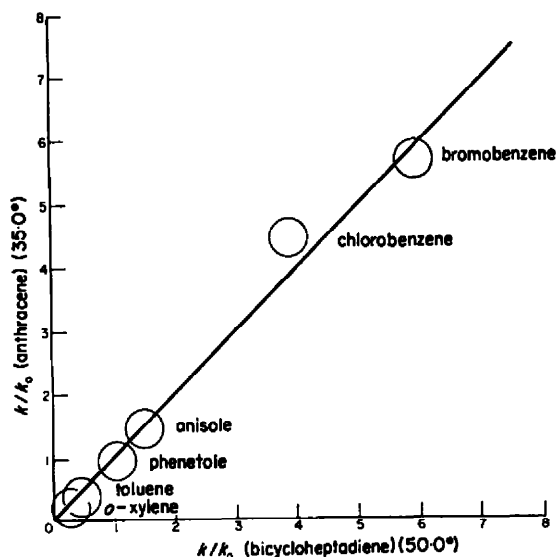
Fig. 1. Rates relative to benzene for TCNE addition to anthracene and
bicycloheptadiene respectively, in aromatic solvents.

A quantitative correlation on these lines is shown in Fig. 3, where the log of the
rate constant for addition of TCNE to B is plotted against $(K_e + 1)^{-1}$, proportional
in dilute solution to the free TCNE not involved in 1:1 complex with the solvent.*
The same plot for A also gives a straight line, of course, with anisole alone lying off
it (Fig. 4).† The measured rate constants in solvents for which values of $K_e$ were
available were then re-calculated, assuming that the rate of reaction of TCNE spe-
cifically $\pi$-complexed with the solvent was negligible compared with the rate of reaction
of TCNE not complexed with the solvent (i.e. all concentrations of TCNE were
divided by ($K_e$[solvent] + 1)). However, as the examples in Table 5 illustrate, the
rate constants were not seriously changed.

\* In the equilibrium

$$T(TCNE) + S(Solvent) \rightleftharpoons C(\pi\text{-complex})$$

$$K_e = \frac{C}{(T - C)(S - C)} = \frac{C}{(T - C)N_s}, \tag{1}$$

concentrations being in mole fractions.
Complexed TCNE = $C = K_e . N_s . T - K_e . N_s . C$

$$= \frac{K_e . N_s . T}{(K_e . N_s + 1)} \tag{2}$$

"Free" TCNE = $(T - C)$ $\qquad = \dfrac{C}{K_e . N_s}$ $\qquad$ from (1)

$$= \frac{T}{(K_e . N_s + 1)} \qquad \text{from (2)}$$

In dilute solution $N_s$ tends to 1, and "free" TCNE becomes proportional to $(K_e + 1)^{-1}$.

† The estimated $K_e$ of 0·49 for $o$-dichlorobenzene was obtained from its solubility for TCNE by
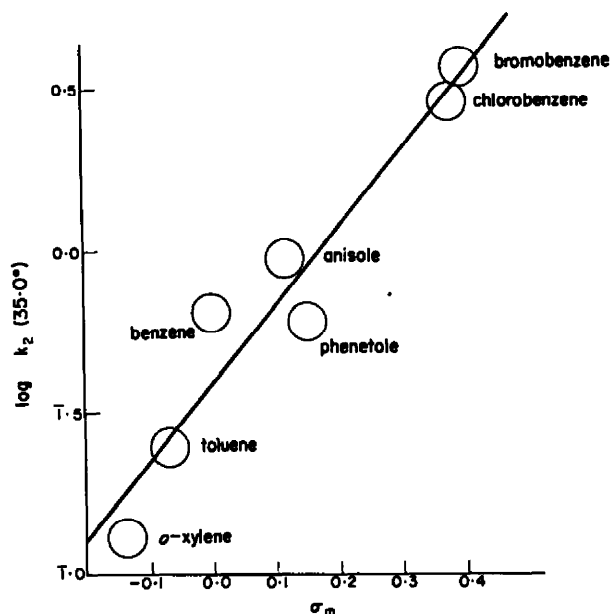extrapolation of the plot in Fig. 5.

FIG. 2. log $k_2$ (TCNE vs. anthracene at 35·0°) related to $\sigma_m$ for aromatic solvents.
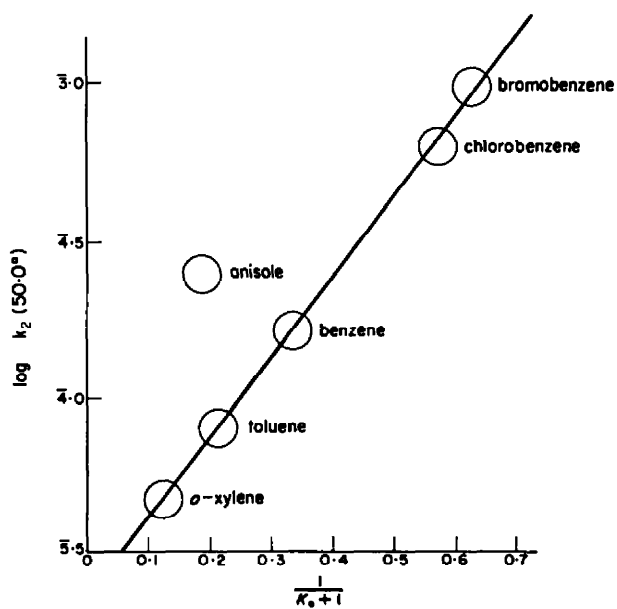


FIG. 3. log $k_2$ for bicycloheptadiene and TCNE related to $K_e$ for TCNE with aromatic solvents.
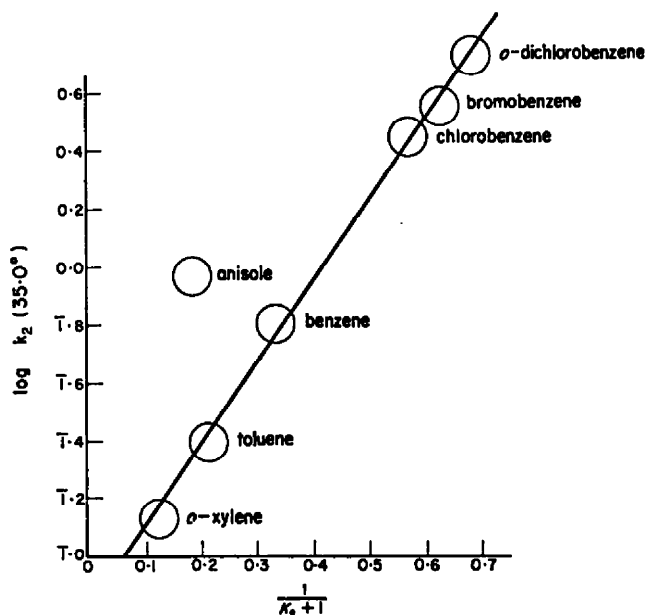
FIG. 4. log $k_2$ for anthracene and TCNE related to $K_c$ for TCNE with aromatic solvents.
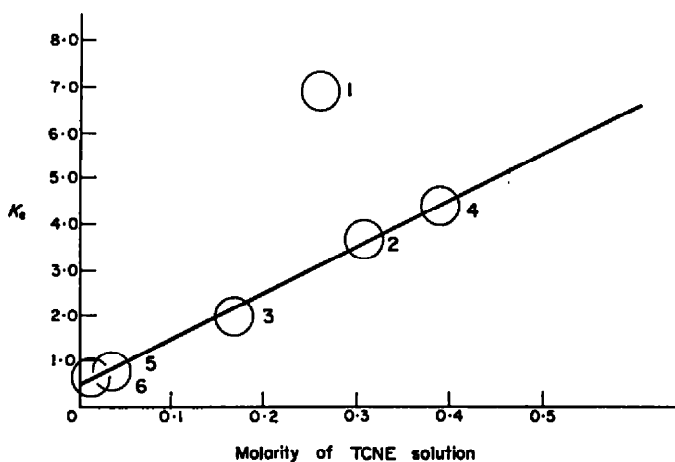


FIG. 5. Solubility of TCNE related to complexing with aromatic solvents.

One can draw reliable conclusions about the polarity of the transition state of a bimolecular reaction from the effect of change of solvent on the rate only if there is some independent measure of the solvation energies of the two reactants in the various solvents. The solubilities of A and of TCNE in the aromatic solvents were therefore determined at a standard temperature (17°) (Table 6). The very slight variation in the solubility of A shows that desolvation of A in the transition state must be a negligible

cause of change of rate with solvent. On the other hand, the solubility of TCNE varies over a range of 50, so that desolvation of TCNE may be an important factor. The solubility of TCNE is exactly proportional to $K_e$ (measured[21] in methylene dichloride solution) with the single exception of o-xylene in which TCNE appears to be much less soluble than expected (Fig. 5). In all the other solvents listed the saturated solution was in equilibrium with crystalline TCNE (the standard state for our comparison), whereas in o-xylene the solid phase was the 1:1 π-complex, which could be separated as deep red crystals that slowly lost o-xylene by evaporation. The figures in Table 6 show that the solubility of "free" TCNE is also proportional to $K_e$.

The column, $N_f$, in Table 6 gives the mole fraction of TCNE in the saturated solution not involved in 1:1 π-complex with the solvent, on the approximation that $K_e$ for the saturated solution is the same as for the dilute solution in methylene dichloride, and that the density of the solution is the same as that of the solvent. Although these assumptions render doubtful the physical significance of the figures, it is interesting that the log of the rate constants for reaction of TCNE with A (at 35°) or B (at 50°) in the solvents varies linearly with the mole fraction of "free" TCNE in the saturated solution for four of the five solvents for which the figures are given in Table 6—with anisole again the exception (too fast). The rates from toluene to bromobenzene vary by a factor of 10, the fastest rate being in the least solvating medium for free TCNE.

Unfortunately many solvents had to be eliminated because of competing solvolysis of TCNE (e.g. dimethylformamide, ethylene carbonate, nitromethane) or negligible solubility[22] (e.g. carbon tetrachloride, tetrachloroethylene, cyclohexane). We are left with too few common solvents for correlation with the ratio of endo to exo isomers in the addition of methyl acrylate to cyclopentadiene[7] (Ω), or the wavelength of the charge-transfer absorption of 1-ethyl-4-methoxycarbonylpyridinium iodide[23a] (Z). However, eleven of our solvents were included in the new $E_T$ scale of Dimroth, Reichardt et al.[23b] (transition energy of the long-wavelength band of 2,4,6,3',5'-pentaphenyl-1-4'-hydroxyphenyl-pyridinium betaine). Although again the more polar solvents (higher $E_T$) tend to produce a faster reaction, a plot of log $k_2$ against $E_T$ shows a very wide scatter.

By using very much higher concentrations of dienophile than is possible with TCNE, Andrews and Keefer[6] showed that in the addition of maleic anhydride to 9,10-dimethylanthracene in chloroform no Diels-Alder adduct was formed by reaction of maleic anhydride with dimethylanthracene π-complexed with maleic anhydride or added citraconic anhydride, but only by reaction of maleic anhydride with un-complexed dimethylanthracene (possibly via the π-complex, which then isomerized). At least in their system, then, π-complexed diene did not react with another dienophile molecule. Evidence has been given above for the complementary proposition that TCNE π-complexed to an aromatic solvent molecule does not react with A or B. The second order kinetics do not, of course, distinguish between the two possible

[21] Cf. G. H. Schenk, M. Santiago and P. Wines, *Analyt. Chem.* **35**, 167 (1963).

[23a] E. M. Kosower, *J. Amer. Chem. Soc.* **80**, 3253 (1958).

[23b] K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, *Liebigs Ann.* **661**, 1 (1963); C. Reichardt *Angew. Chem.* **77**, 30 (1965).

reaction paths (i) in which the diene-TCNE $\pi$-complex is an intermediate, and (ii) in which it is not:

$$A + TCNE \underset{}{\overset{\text{fast}}{\rightleftharpoons}} [A \rightarrow TCNE] \xrightarrow{\text{slow}} I \qquad (i)$$

$$I \xleftarrow{\text{slow}} A + TCNE \underset{}{\overset{\text{fast}}{\rightleftharpoons}} [A \rightarrow TCNE] \qquad (ii)$$
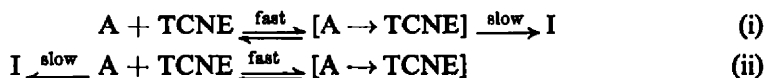
The equilibrium constant for $\pi$-complexing of TCNE with A or B is not known, but correlation of the values of $K_s$ for a range of aromatic hydrocarbons with TCNE and chloranil[24] gives an estimated value of about 29 for the A-TCNE $\pi$-complex in carbon tetrachloride ($\lambda_{max}$741 and 465 m$\mu$): the relation of $\Delta F°$ with ionization potential[21] gives a value of 38 for $K_s$, taking 7·74 eV as the ionization potential of anthracene.[16b] At the dilutions used for the kinetic measurements most of the A (and certainly B) would have been uncomplexed. Nevertheless, the geometry of the A-TCNE $\pi$-complex in the conformation in which the olefinic carbon atoms of the TCNE lie on the plane through $C_9$ and $C_{10}$ of the A molecule is so similar to that of the adduct as to make it an almost inevitable intermediate (as many have pointed out before). For A this conformation should be the most favoured, or at least one of the most favoured, probably with little impediment to interconversion with other parallel-plane arrangements, e.g. the conformation with the TCNE double bond at right angles to the line through $C_9$ and $C_{10}$, not directly convertible into the adduct. (For B, on the other hand, the most stable $\pi$-complex would probably be the one with TCNE co-ordinated on to one double bond of the diene from the *exo* side.) This $\pi$-complex could pass into the adduct by three routes*, all of which have been considered in other cases:

    (a) by a single, symmetrical transition state with both new bonds equal in length (III; $1 - 9 = 2 - 10$);

    (b) by a single, unsymmetrical transition state with one new bond shorter than the other (III; $1 - 9 < 2 - 10$, and $C_1$ and $C_9$ rehybridized more than $C_2$ and $C_{10}$);

    (c) through an intermediate dipole (IV).

[In the case where the dipole (IV) is present only in low stationary concentration, being rapidly converted into product I, progressive overlap of the $\delta^-$ p-orbital on $C_2$ and the $\delta^+$ p-orbital on $C_{10}$ with concomitant rehybridization of $C_2$ and $C_{10}$ from $sp^2$ towards $sp^3$ in the transition state for formation of IV converts the two-step mechanism (c) into a one-step mechanism (b).]

Kinetic methods alone cannot distinguish these possibilities with certainty. The extreme form of the two-step mechanism (c) in which the dipolar intermediate (IV) might be formed faster than it cyclizes to the adduct (I) (cf. TCNE + dimethyl-aniline[25]) has been excluded by observation of the UV and visible spectra of solutions of TCNE and A in ethyl acetate. Carbonium ion-anion pairs are expected to have very nearly the same spectra as the free ions, so that the dipole (IV) should absorb rather like protonated anthracene ($\lambda_{max}$425 m$\mu$, $\epsilon$ 31,000 in $H_2SO_4$)[26] with perhaps an intramolecular charge-transfer band added. No absorption could be detected during the reaction beyond that due to the reactants and the TCNE-A $\pi$-complex.

    * A precisely analogous series of mechanisms is possible, of course, for addition of TCNE to B.

[24] G. Briegleb, J. Czekalla and G. Ruess, *Z. phys. Chem.* **30**, 316 (1961).

[25] Z. Rappoport, *J. Chem. Soc.* 4498 (1963); P. G. Farrell and J. Newton, *Tetrahedron Letters* 189 (1964).

[26] V. Gold and F. L. Tye, *J. Chem. Soc.* 2172 (1952).

TABLE 1. ADDITION OF ANTHRACENE TO TETRACYANOETHYLENE

| Solvent (Dielectric constant)* | Temp (°C) | Mean $k_2$ (1 mole$^{-1}$ sec$^{-1}$) | $\Delta H\ddagger$ ($\pm 0.5$ Kcal mole$^{-1}$) | $\Delta S\ddagger$ ($\pm 2.0$ e.u.) |
|---|---|---|---|---|
| Chloroform (4·81) | 0·2 | 2·55 | | |
| | 10·0 | 3·63 | 4·25 | −49 |
| | 20·0 | 4·77 | | |
| | 30·0 | 6·28 | | |
| Cyclohexanone (18·3) | 0·1 | 0·0405 | | |
| | 10·0 | 0·0819 | 9·7 | −29 |
| | 20·0 | 0·154 | | |
| | 30·1 | ·0·260 | | |
| Methylacetate (6·68) | 0·1 | 0·102 | | |
| | 10·0 | 0·174 | 7·5 | −35 |
| | 20·0 | 0·281 | | |
| | 30·0 | 0·457 | | |
| Ethylacetate (6·02) | 0·20 | 0·0557 | | |
| | 10·0 | 0·0975 | 9·0 | −31 |
| | 20·0 | 0·181 | | |
| | 30·1 | 0·310 | | |
| Acetonitrile (37·5) | 0·5 | 0·653 | | |
| | 10·0 | 1·07 | | |
| | 19·9 | 1·73 | 7·3 | −37 |
| | 30·0 | 2·71 | | |
| Propionitrile (27·2) | 30·0 | 1·09 | | |
| | 40·0 | 1·69 | 7·0 | −36 |
| | 50·0 | 2·39 | | |
| Ethylene dichloride (10·4) | 30·0 | 4·69 | | |
| | 40·0 | 6·62 | 6·45 | −42 |
| | 50·0 | 9·66 | | |
| Propylene carbonate (61·7) | 30·0 | 1·94 | | |
| | 40·0 | 2·84 | 7·1 | −38 |
| | 50·0 | 4·28 | | |
| Sulpholane (44) | 30·0 | 2·74 | | |
| | 40·0 | 3·80 | 6·0 | −42 |
| | 50·0 | 5·39 | | |
| Aromatic solvents | | | | |
| o-Xylene (2·57) | 30·0 | 0·0900 | | |
| | 40·0 | 0·184 | 12·3 | −23 |
| | 50·0 | 0·341 | | |
| Toluene (2·38) | 35·0 | 0·247 | | |
| | 45·0 | 0·458 | 11·0 | −26 |
| | 55·0 | 0·785 | | |
| Benzene (2·28) | 25·0 | 0·382 | | |
| | 35·0 | 0·640 | 9·2 | −30 |
| | 45·0 | 1·08 | | |
| Chlorobenzene (5·62) | 25·0 | 1·81 | | |
| | 35·0 | 2·86 | | |
| | 45·0 | 4·27 | 7·5 | −36·5 |
| | 25·0 | 2·29 | | |

TABLE 1 (Continued)

| Solvent (Dielectric constant)* | Temp (°C) | Mean $k_2$ (1 mole$^{-1}$ sec$^{-1}$) | $\Delta H\ddagger$ ($\pm 0.5$ Kcal mole$^{-1}$) | $\Delta S\ddagger$ ($\pm 2.0$ e.u.) |
|---|---|---|---|---|
| Bromobenzene | 35.0 | 3.66 | 7.4 | −37 |
| (5.40) | 45.0 | 5.36 | | |
| | 25.0 | 4.00 | | |
| o-Dichloro- | 30.0 | 4.65 | | |
| benzene | 35.0 | 5.28 | 4.5 | −47 |
| (9.93) | | | | |
| | 25.0 | 0.583 | | |
| Anisole | 35.0 | 0.944 | 8.1 | −32 |
| (4.33) | 45.0 | 1.47 | | |
| Phenetole | 35.0 | 0.604 | — | — |
| (4.22) | | | | |

* A. Weissberger, "*Technique of Organic Chemistry*" Vol. 7. Interscience, New York (1955). P. L. Kronick and R. M. Fuoss, *J. Amer. Chem. Soc.* **77**, 6114 (1955); R. Kempa and W. H. Lee, *J. Chem. Soc.* 1936 (1958); C. H. Langford and R. L. Burwell, *J. Amer. Chem. Soc.* **81**, 3799 (1959); E. M. Arnett and C. F. Douty, *Ibid* **86**, 409 (1964).

TABLE 2. ADDITION OF BICYCLOHEPTADIENE TO TETRACYANOETHYLENE

| Solvent | Temp (°C) | Mean $k_2(\times 10^4)$ (1 mole$^{-1}$ sec$^{-1}$) | $\Delta H\ddagger$ ($\pm 0.5$ Kcal mole$^{-1}$) | $\Delta S\ddagger$ ($\pm 2.0$ e.u.) |
|---|---|---|---|---|
| | 50.0 | 0.478 | | |
| o-Xylene | 60.1 | 1.05 | 17.5 | −24 |
| | 70.1 | 2.50 | | |
| | 50.0 | 0.807 | | |
| Toluene | 60.1 | 1.98 | 16 | −29 |
| | 70.1 | 3.55 | | |
| | 40.1 | 0.783 | | |
| Benzene | 50.1 | 1.67 | 15 | −30.5 |
| | 60.6 | 3.54 | | |
| | 40.0 | 3.19 | | |
| Chlorobenzene | 50.0 | 6.47 | | |
| | 60.1 | 12.5 | 13.5 | −32 |
| | 40.0 | 4.77 | | |
| Bromobenzene | 50.0 | 9.89 | 13.8 | −30 |
| | 60.1 | 19.3 | | |
| | 40.0 | 1.18 | | |
| Anisole | 50.0 | 2.53 | 14.2 | −31 |
| | 60.1 | 5.01 | | |
| Phenetole | 50.0 | 1.77 | — | — |

TABLE 3. DISSOCIATION OF ANTHRACENE-TETRACYANOETHYLENE ADDUCT

| Solvent | Temp (°C) | Mean $k_1(\times 10^5)$ (sec$^{-1}$) | $\Delta H\ddagger$ ($\pm 0.5$ Kcal mole$^{-1}$) | $\Delta S\ddagger$ ($\pm 2.0$ e.u.) |
|---|---|---|---|---|
| | 40.1 | 1.03 | | |
| Methanol | 50.1 | 3.76 | 24.9 | −2 |
| | 60.0 | 12.0 | | |
| | 39.9 | 1.31 | | |
| Ethanol | 50.0 | 5.36 | 27.1 | +6 |
| | 60.0 | 19.5 | | |
| | 40.1 | 1.24 | | |
| Dioxan | 50.1 | 5.16 | 27.5 | +7 |
| | 60.6 | 20.0 | | |

TABLE 4. RELATIVE RATES OF ADDITION OF ANTHRACENE AND
BICYCLOHEPTADIENE TO TETRACYANOETHYLENE

| Solvent | Anthracene | | Bicycloheptadiene | |
|---|---|---|---|---|
| | $k_2(35 \cdot 0^\circ)$ | $k/k_0$ | $k_2(\times 10^4)(50 \cdot 0^\circ)$ | $k/k_0$ |
| Benzene | 0·640 | — | 1·67 | — |
| Toluene | 0·247 | 0·386 | 0·807 | 0·483 |
| o-Xylene | 0·130 | 0·203 | 0·478 | 0·286 |
| Anisole | 0·944 | 1·47 | 2·53 | 1·51 |
| Phenetole | 0·604 | 0·944 | 1·77 | 1·06 |
| Chlorobenzene | 2·86 | 4·47 | 6·47 | 3·87 |
| Bromboenzene | 3·66 | 5·72 | 9·89 | 5·92 |

TABLE 5. SECOND ORDER RATE CONSTANTS FOR REACTION
OF BICYCLOHEPTADIENE WITH TETRACYANOETHYLENE
AT $50 \cdot 0^\circ$ ($\times 10^4$ in 1 mole $^{-1}$sec$^{-1}$)

| Solvent | Measured $k_2$ | Corrected $k_2$ |
|---|---|---|
| o-Xylene | 0·478 | 0·418 |
| Toluene | 0·807 | 0·698 |
| Benzene | 1·67 | 1·58 |
| Anisole | 2·53 | 2·23 |
| Chlorobenzene | 6·47 | 6·00 |
| Bromobenzene | 9·89 | 9·41 |

TABLE 6. SOLUBILITY OF ANTHRACENE AND OF TETRACYANOETHYLENE IN AROMATIC
SOLVENTS AT 17°

| Solvent | A[a] | TCNE[a] | $K_c$ | $N_s$[b] | "Free" TCNE[c] | $\pi$-Complexed TCNE[e] | $N_f$[d] | Total moles[e] per 1 | % TCNE "free" |
|---|---|---|---|---|---|---|---|---|---|
| 1. o-Xylene | 0·067 | 0·259 | 6·97 | — | — | — | — | — | — |
| 2. Toluene | 0·067 | 0·307 | 3·70 | 0·968 | 0·067 | 0·240 | 0·00689 | 9·73 | 22 |
| 3. Benzene | 0·073 | 0·165 | 2·00 | 0·986 | 0·055 | 0·110 | 0·00481 | 11·4 | 33·5 |
| 4. Anisole | 0·112 | 0·390 | 4·42 | 0·960 | 0·074 | 0·316 | 0·00768 | 9·64 | 19 |
| 5. Chloro-benzene | 0·084 | 0·031 | 0·77 | 0·997 | 0·018(5) | 0·013(5) | 0·00188 | 9·86 | 59·5 |
| 6. Bromo-benzene | 0·084 | 0·012 | 0·61 | 0·999 | 0·007(5) | 0·005(5) | 0·00078 | 9·56 | 62·5 |
| 7. o-Dichloro-benzene | 0·090 | 0·008 | — | — | — | — | — | — | — |

[a] Molarity in saturated solution.
[b] Mole fraction of solvent in solution saturated with TCNE.
[c] Molarity of TCNE in saturated solution not involved in 1:1 $\pi$-complex with solvent.
[d] Mole fraction of "free" TCNE.
[e] TCNE and solvent.

Over the range of solvents from *o*-xylene to chloroform the rate of reaction of TCNE with A increases by a factor of 70: the acceleration produced by changing from benzene to chloroform ($\times$ 11) is nearly twice the acceleration in the reaction of *p*-benzoquinone with cyclopentadiene produced by the same change in solvent[19,27] ($\times$ 6). Although the two charges in IV would be well dispersed internally, the sensitivity to solvent seems too small to allow a transition-state on the way to such a dipole with only electrostatic attraction between the two charges (significant overlap of the orbitals would shift the mechanism to b). The data are consistent with the direct, symmetrical conversion of the $\pi$-complex into the adduct through a polarized transition state (a), though there is nothing to exclude the unsymmetrical mechanism (b).

The effect of deuterium at 9 and at 9 and 10 in A will soon be reported.[16]

## EXPERIMENTAL

*Purification of TCNE.* The method of Merrifield and Phillips[21] was used, which gave a colourless crystalline solid, m.p. 198–200° (sealed tube), with the reported IR spectrum,[28] which was stored under vacuum. (Found: C, 56·21; N, 43·76; Calc. for $C_6N_4$: C, 56·26; N, 43·74%.)

*Purification of anthracene.* The chromatographic method recommended by Vogel[29] was employed, on B.D.H. Blue Fluorescent anthracene. Subsequent recrystallization from purified EtOH afforded white leaflets with blue fluorescence, m.p. 218–219°. Samples were stored in brown glass bottles, kept in the dark in a vacuum desiccator.

*Purification of bicyclo[2,2,1]hepta-2,5-diene.* The crude yellow Shell material was washed 3 times with $NaHCO_3$ aq, and to neutrality with portions of distilled water. The final separation was improved by the use of ether, preliminary drying being effected with anhydrous $Na_2SO_4$, and lastly with two portions of anhydrous $CaSO_4$ (Drierite). Decantation of the liquid was followed by two fractional distillations (2 × 30 cm Fenske column) under dry $N_2$, collecting the middle third fraction each time (b.p.$_{758}$ = 89–90°) as a colourless liquid. It was stored under dry $N_2$ in the dark, and had spectra as follows:—IR (neat) −735(s), 1315(m), 1545(w), 2890(w), 2960(w), 3000(m), 3100(w) cm.$^{-1}$; NMR[30] ($CCl_4$)–$\tau$ values 3·36 (4-proton triplet), 6·49 (2-proton septet) and 8·06 (2-proton triplet). A sample submitted to VPC analysis (under the same conditions as the solvents) showed only a single peak.

*Purification of solvents*

Weissberger[31] was used as a general guide. All solvents were fractionally distilled through a 3 × 50 cm Fenske column immediately before use.

(a) *Benzene.* B.D.H. Analar benzene was washed with 3 portions of conc. $H_2SO_4$, with water, and then with dil. NaOH aq until neutral, followed again by water. After drying with finely ground $CaH_2$, followed by refluxing over two or three fresh samples of $P_2O_5$, the solvent was distilled and finally fractionated in rigorously dried apparatus. This method was used for all the aromatic solvents except anisole and phenetole,[21] starting from the purest available commercial grade.

(b) *Dioxan.* All operations were conducted under dry $N_2$. The solvent was passed down a column of activated alumina (300°/24 hr), a ratio of 1 g per ml being used, and then refluxed for 48 hr over Na. Distillation was followed by fractionation, the purified dioxan being stored under dry $N_2$, and used within 2–3 days.

(c) *Acetonitrile.* Preliminary distillation was followed by refluxing over 3 portions of fresh $P_2O_5$ for 24 hr each. The solvent was then refluxed over finely divided $CaH_2$ for the same time, distilled and finally fractionated. This method was also used for propionitrile.

(d) MeOH and EtOH were dried[38] and then fractionally distilled. AnalaR methyl and ethyl

[27] W. Rubin, H. Steiner and A. Wassermann, *J. Chem. Soc.* 3046 (1949).
[28] C. E. Looney and J. R. Downing, *J. Amer. Chem. Soc.* **80**, 2840 (1958).
[29] A. I. Vogel, *Practical Organic Chemistry* p. 944. Longmans Green, London (1957).
[30] F. S. Mortimer, *J. Mol. Spec.* **3**, 528 (1959).
[31] A. Weissberger, *Technique of Organic Chemistry* Vol. 7. Interscience, New York (1955).
[32] H. Lund and J. Bjerrum, *Ber. Dtsch. Chem. Ges.* **64**, 210 (1931).

acetate were shaken with $K_2CO_3$, treated with $CaCl_2$ and fractionated.[33] Sulpholane was twice fractionated under $N_2$ at 3 mm. $CHCl_3$,[31] $CCl_4$,[31] tetrachloroethylene,[31] 1,2-dichlorethane,[31] propylene carbonate,[34] cyclohexanone,[35] acetone,[36] nitromethane[37] and dimethylformamide[38] were purified by published methods.

*Water content of the purified solvents.* In view of the susceptibility of TCNE to hydrolysis, solvents were dried as thoroughly as possible. However, even in the driest of them, the solutions for the anthracene runs contained the same order of molarity of water as of reactants. The rate of hydrolysis of TCNE in such a solution was checked by measuring the UV spectrum of the dienophile (in aromatic solvents, the charge-transfer spectrum[31]) after known time intervals, and found to be completely negligible for the anthracene case, where the rate of the Diels-Alder reaction is relatively rapid, and for bicycloheptadiene, where approximately $5 \times 10^2$ more concentrated solutions of TCNE were used. For the following solvents, this method detected competing solvolysis of TCNE, and they were not employed for kinetic measurements: acetone, nitromethane, dimethylformamide, ethylene carbonate.

Karl Fischer titration was used to determine the water content of each solvent, under standard conditions with an equal volume (5 ml) of preneutralized MeOH, to a potentiometric end-point with a Townson and Mercer instrument.

| Solvent | Water (wt %) | Solvent | Water (wt %) |
|---|---|---|---|
| Methanol | 0·001 | Chlorobenzene | 0·006 |
| Ethanol | 0·006 | Bromobenzene | 0·01 |
| Dioxan | 0·01 | Anisole | 0·02 |
| Benzene | 0·005 | Phenetole | 0·008 |
| Toluene | 0·01 | o-Dichlorobenzene | 0·002 |
| o-Xylene | 0·008 | Methyl acetate | 0·01 |
| Ethyl acetate | 0·007 | Acetonitrile | 0·005 |
| Cyclohexanone | 0·009 | Propionitrile | 0·009 |
| Acetone | 0·01 | Dimethylformamide | 0·007 |
| Chloroform | 0·005 | Ethylene carbonate | 0·01 |
| 1,2-Dichloroethane | 0·006 | Propylene carbonate | 0·006 |
| Tetrachloroethylene | 0·008 | Sulpholane | 0·009 |
| Carbon tetrachloride | 0·005 | | |

The remaining suitable solvents were analysed further by VPC, using a Perkin-Elmer Model 451 Fractometer with thermistor detector, and a 6 ft polyethylene glycol (K) column operating at 65°. In no case was any subsidiary peak of greater than 1 % observed.

*Thermostats.* Two types of thermostat were used, depending on the concentration of the reactant whose concentration was being followed: (a) A Townson and Mercer thermostat bath (S.770), water-filled, with a specified temp control of ±0·01°. For runs at temp lower than 10°, ice-water was circulated through the outer cooling jacket. (b) An Adkins Type B thermostatted cell-holder, fitted directly to the Unicam SP.500 spectrometer used throughout this work. Temp control of ±0·02° is claimed, but at least 2 hr stabilization time is required for this to be achieved. In both methods, temperatures were measured on a common thermometer, calibrated to 0·2°, and corrected using an N.P.L. 0–100° standard.

*Kinetic procedure*

The concentration of either anthracene or TCNE was followed throughout each run.

*Method* (a) the methanol dilution technique. Solutions were made up in 25 or 50 ml graduated flasks, and equilibrated at the bath temp for not less than 30 min. Equal vol (10 ml) of each reactant

[33] Cf. C. J. Haggerty and J. F. Weiler, *J. Amer. Chem. Soc.* **51**, 1623 (1929).
[34] P. L. Kronick and R. M. Fuoss, *J. Amer. Chem. Soc.* **77**, 6114 (1955); R. Kempa and W. H. Lee, *J. Chem. Soc.* 1936 (1958).
[35] R. W. Crowe and C. P. Smyth, *J. Amer. Chem. Soc.* **73**, 5406 (1951).
[36] G. S. Hammond, M. F. Hawthorne, J. H. Waters and B. M. Graybill, *J. Amer. Chem. Soc.* **82**, 704 (1960).
[37] H. Van Looy and L. P. Hammett, *J. Amer. Chem. Soc.* **81**, 3872 (1959).
[38] G. H. Brown and R. Al-Urfali, *J. Amer. Chem. Soc.* **80**, 2113 (1958).

solution were then transferred by bath-temp pipette to duplicate thermostatted reaction vessels (50 or 100 ml B10 glass-stoppered, round-bottomed flasks), and thoroughly mixed by shaking, zero time being taken when the second reactant solution was half added. A standard Smiths stop-clock, with full second hand sweep, was used for timing. After known intervals of time, aliquots (1 or 2 ml) were withdrawn from each reaction flask, using bath-temp pipettes and a Shandon Pumpette, and quenched in 50 ml graduated flasks containing MeOH (except in the case of aromatic solvents), which immediately stops the addition reaction. After 10–15 min, the solutions were made up to the mark with MeOH, mixed thoroughly by shaking, and then their optical densities immediately determined on the UV spectrometer, using an appropriate MeOH/solvent blank. The same pair of matched Spectrosil quartz cells was used throughout.

For anthracene, the following wavelengths were used:—251·2, 324·5, 340·5, 357·5, 376·0 m$\mu$.

With aromatic solvents, quenching was effected by dilution with the particular solvent in each case, and the TCNE charge-transfer peak monitored at the following wavelengths:

> 430 m$\mu$—benzene, chlorobenzene, o-dichlorobenzene;
> 440 m$\mu$—toluene, bromobenzene;
> 480 m$\mu$—o-xylene;
> 507 m$\mu$—anisole;
> 510 m$\mu$—phenetole.

These wavelengths were selected as being as close to $\lambda_{max}$ as possible, but so that the optical densities measured were not detectably enhanced by TCNE/anthracene charge-transfer.

In all cases, optical density values were converted to concentrations by the use of calibration plots, constructed employing the same purified materials.

*Method* (b) the thermostatted cell technique. Solutions were prepared in 25 ml graduated flasks (with the aid of a 5-place balance), and equilibrated in a thermostat as before. Equal volumes were then transferred to a sample cell, maintained at reaction temp within the cell compartment of the spectrometer, zero time again being taken when the second component was half added. Direct optical density measurements were made after known time intervals, against an appropriate solvent blank. A second duplicate run was performed immediately after the first on the same reactant solutions. For anthracene runs in non-aromatic solvents, method (a) was used, and for anthracene and bicycloheptadiene kinetics in aromatic solvents, method (b).

*Treatment of kinetic data.* The addition reactions were assumed to be second order, and plots of log (a − x)/(b − x) vs. time gave excellent straight lines up to at least 30% reaction, in all cases except for the solvents

$$\log (a - x)/(b - x) = t[k_2(a - b)]/2·303 + \log a/b$$

acetonitrile, toluene (55°) and o-xylene. This was due to competing solvolysis in the case of acetonitrile, and reversibility in the two aromatic solvents. Bicycloheptadiene gave linear second order plots in all the solvents used, reflecting the irreversibility of the addition reaction with this diene.

The anthracene adduct dissociation was assumed to be first order, and plots of time against log (a − x) were linear up to approximately 20%

$$t = (2·303/k_1) \log a - (2·303/k_1) \log (a - x)$$

reaction in the three solvents used. Subsequent curvature was attributed to solvolysis of TCNE with ethanol and methanol, and reversibility with dioxan.

*Arrhenius parameters.*

$$\log k = \log A - (E_a/2·303RT)$$

For each solvent except phenetole, runs were conducted at not less than three temp, ideally no closer than 10 degree intervals. log $k$ was plotted against 1/T, and $E_a$ and log A obtained from the slope and intercept of the graph. These quantities were converted into $\Delta H$ and $\Delta S$ values respectively.[39]

*Attempted estimation of TCNE.* Some effort was expended initially in attempts to develop a simple quantitative technique for the estimation of TCNE in organic solvents. One semi-quantitative method was available,[40] using N,N-dimethylaniline to form a highly coloured derivative, but this was found

[39] J. F. Bunnett in Ref. 31, Vol. 8, Part I (2nd Edition), p. 199.

[40] B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *J. Amer. Chem. Soc.* **80**, 2806 (1958).

to be only successful using solid samples, the rate of formation[36] and the extinction coefficient of the dye depending strongly on the solvent. Similar approaches using 2,6-dimethylphenol,[41] and hydrogen iodide reduction[42] followed by iodine estimation, also proved unsuitable. A more promising method seemed to be the alkaline hydrolysis of TCNE.[43] Determination of cyanide ion, however, could not be effected quantitatively by a sufficiently simple method. Volhard titration was unsuitable for organic solvents, and needed relatively high concentrations, whereas the normally highly sensitive ferroin technique was too tedious, and again irreproducible in any solvents except water and aqueous lower alcohols.

*Solubility.* Weighed portions of finely ground anthracene or tetracyanoethylene were added to a known volume of purified solvent, shaken mechanically for a constant time at 17° until a visible turbidity showed the solution was saturated.

[41] A. E. Schilt, *Analyt. Chem.* **30**, 1409 (1958).
[42] W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *J. Amer. Chem. Soc.* **80**, 2783 (1958).
[43] W. J. Middleton and V. A. Engelhardt, *J. Amer. Chem. Soc.* **80**, 2788 (1958).