961. *Complex Formation in Pyridine Solutions of Aromatic Polynitro-hydrocarbons.*

By R. E. MILLER and W. F. K. WYNNE-JONES.

Complex-formation in pyridine solutions of 1,3,5-trinitrobenzene has been studied in detail and equilibrium and kinetic data are presented. Two reactions occur, the first reversible and the second irreversible. Conductivity measurements show that both reactions lead to ionic species. The slow changes in similar systems involving 2,4,6-trinitrotoluene and 2,4,6-trinitro-*m*-xylene are also reported.

IN a previous paper [1] we showed that *s*-trinitrobenzene dissolves in a number of aliphatic amines, giving at once solutions whose red colour is associated with an absorption band at 450—475 mμ. When *s*-trinitrobenzene is dissolved in pyridine a similar band is observed near 465 mμ, but the colour is formed slowly and is much less intense than that of diethylamine solutions containing the same trinitrobenzene concentration, which suggests that the equilibrium constant for the reaction is low. An additional absorption band near 570 mμ occurs only in solvents of relatively high dielectric constant.[1]

A slow secondary reaction producing an absorption band at about 514 mμ is also observed in solvents of high dielectric constant [1] though not in purified aliphatic amines.

Slow conductivity changes also occur in these solutions. Hantzsch and Caldwell [2] observed small electrical conductivities for pyridine solutions of *s*-trinitrobenzene and Davies [3] noted slow changes in electrical conductivity for which he found a unimolecular velocity constant.

The present paper describes the evaluation of kinetic and equilibrium results from light-absorption measurements that are correlated also with changes in electrical conductivity.

EXPERIMENTAL AND RESULTS

The apparatus used for the measurement of light absorption and that for determining electrical conductivity, and the purification of the nitro-compounds have been described elsewhere.[1]

In early measurements " AnalaR " pyridine for use as a solvent was refluxed over sodium hydroxide and distilled, the middle fraction being retained. Solutions of *s*-trinitrobenzene in pyridine purified by this method showed a marked induction period before development of colour. On further purification the induction period disappeared or become negligible.

The measurements recorded here have been obtained for " AnalaR " pyridine which had been refluxed for 3 hr. over barium oxide, then kept over this same oxide before being fractionated in a spinning-band column of high efficiency. The fraction of b. p. 114·0—114·4° was collected, stored in a flask fitted with soda-lime guard-tubes, and kept in the dark. When this pyridine was left for some months before use the induction period reappeared, perhaps owing to an impurity formed by the action of light or oxygen.

A few measurements were carried out in the absence of oxygen. Pyridine was distilled on to the solute in a vacuum, and nitrogen purified by passage through columns of silica gel, soda-lime, and active copper was allowed to enter the apparatus. After 90 min. the spectrum was measured and a second sample was analysed after about 3½ hr.

Results.—The spectrum of a typical solution at various times after mixing is shown in Fig. 1, and the variation with time of the optical density at the three maxima in Fig. 2a. The bands at 465 and 570 mμ follow one another closely and the ratio D_{570}/D_{470} remains constant except for an overlap effect produced by building-up of the product of the secondary reaction.

Curves for the variation with time of the " true " optical density, D', are shown in Fig. 2b. By the " true " optical density we mean that portion of the observed optical density due to the

---

[1] Miller and Wynne-Jones, *J.*, 1959, 2375.
[2] Hantzsch and Caldwell, *Z. phys. Chem.*, 1908, **61**, 228.
[3] Davies, *Trans. Faraday Soc.*, 1935, **31**, 1561.

species having its absorption maximum at the wavelength under consideration. This is smaller than the measured value by an overlap correction which can be estimated.

It is assumed that

$$D_{465} = D'_{470} + aD'_{514}\ (a \approx 0{\cdot}1), \tag{1}$$

and

$$D_{514} = D'_{514} + bD_{465}\ (b \approx 0{\cdot}31), \tag{2}$$

where D refers to the observed optical density and a and b are constants. These assumptions are not strictly valid but the errors introduced are small.

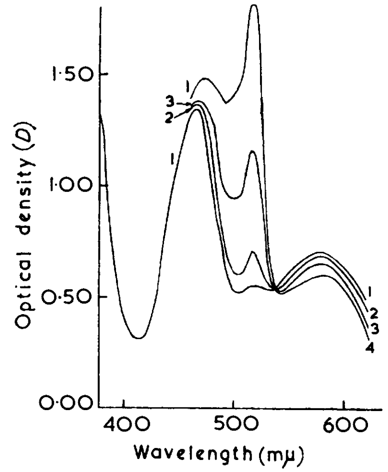

FIG. 1. Absorption spectrum of a typical solution (0·31M) of 1,3,5-trinitrobenzene in pyridine (cell thickness 0·5 cm.).

Times after mixing: (1) 25—45 min. (2) 50—69 min. (3) 140—168 min. (4) 294—316 min.

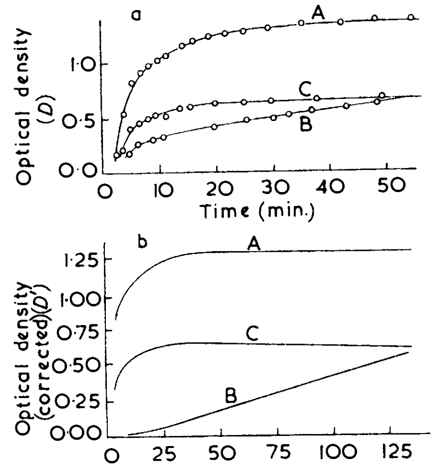

FIG. 2. (a) Variation of optical density with time for a typical solution (0·019M) of 1,3,5-trinitrobenzene in pyridine. (b) The same after correction for overlap.

A, 470 mμ. B, 514 mμ. C, 570 mμ.

Estimates of a and b are obtained by resolving spectra such as those in Fig. 1 into three separate bands above 400 mμ. The two bands having peaks at 470 mμ and 570 mμ are assumed to be symmetrical about their peak frequency; the third is obtained by difference. Fig. 2b indicates the occurrence of two consecutive reactions. Most measurements on the primary reaction have been made at 570 mμ where overlap corrections could be neglected.

To interpret the data for the primary reaction it is convenient to separate the effects of the two reactions. The observed value of D_{570} will be lower than if no secondary reaction had occurred as the latter involves destruction of the primary product. The value of the optical density D'' which would have been observed if no secondary reaction had occurred can be estimated. This is larger than the observed value D by an amount ΔD. It was found that $\mathrm{d}\Delta D_{570}/\mathrm{d}t = k'D_{570}$, so that $\Delta D_{570} = k'\int D_{570}\,.\,\mathrm{d}t$. The correction can thus be obtained from a knowledge of k' and the area under the D_{570}–t curve. It is small and its effect is to hold D'' steady after the observed value begins to drop. These steady values of D'' ($D''_{\mathrm{eq.}}$) are plotted against *s*-trinitrobenzene concentration in Fig. 3. The curves of D'' against t are used to obtain kinetic data.

Measurements of the slope of curves such as B in Fig. 2b give the rate of formation of the secondary product. This is found to be proportional to D_{570}. The measurements carried out in an atmosphere of purified nitrogen indicated that the secondary reaction proceeded in the absence of oxygen.

Curves of specific conductivity against time initially resemble curves A and C of Fig. 2b: instead of reaching a maximum they continue to rise in a roughly linear manner, and the measurements indicate that both primary and secondary products are ionic. The relation

$$\kappa = A'D_{570} + B'D_{514} \tag{3}$$

is obeyed over a considerable range of time for a given solution: a typical conductivity curve is shown in Fig. 4a and is correlated with light absorption measurements in Fig. 4b. The agreement is good for 10—120 min., times which include the initial steep rise and the subsequent slow increase. The values of A' and B' show some scatter when determined for different solutions, presumably because they are very sensitive to traces of moisture.

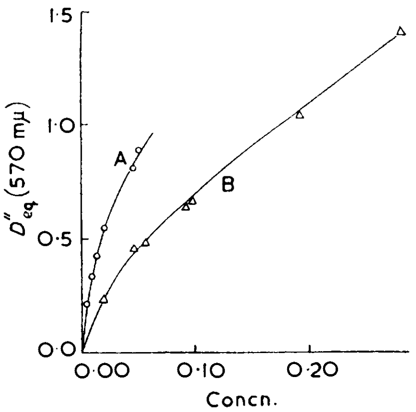

FIG. 3. Variation of equilibrium optical density with trinitrobenzene concentration (mole l.$^{-1}$) (cell thickness 0·5 cm.).

A, At 25·0°. B, At 39·7°.

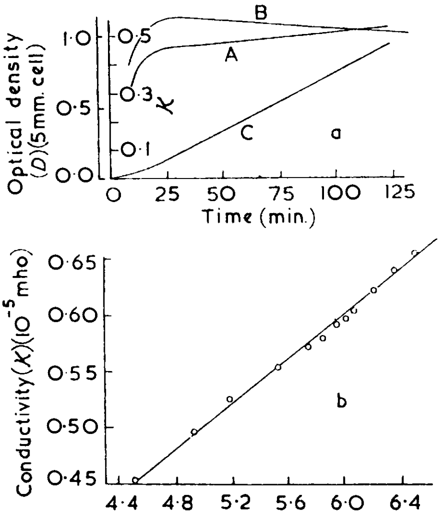

FIG. 4. Variation of electrical conductivity (κ in 10^{-5} mho) with (a) time and (b) optical density (cell thickness 0·5 cm.).

A, Conductivity. B, Optical density at 570 mμ. C, Optical density at 514 mμ.

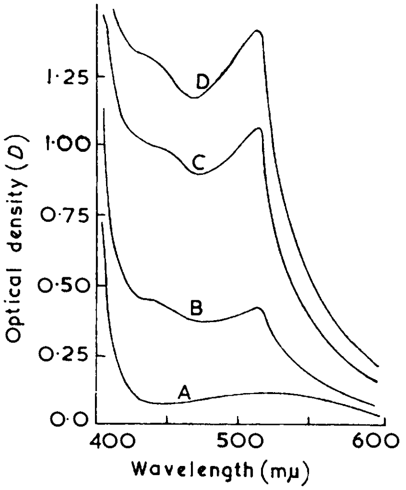

FIG. 5. Spectrum of a typical solution (0·057M) of 2,4,6-trinitrotoluene in pyridine (cell thickness 0·5 cm.).

Times after mixing: A, 40 min. B, 2800 min. C, 8800 min. D, 13,000 min.

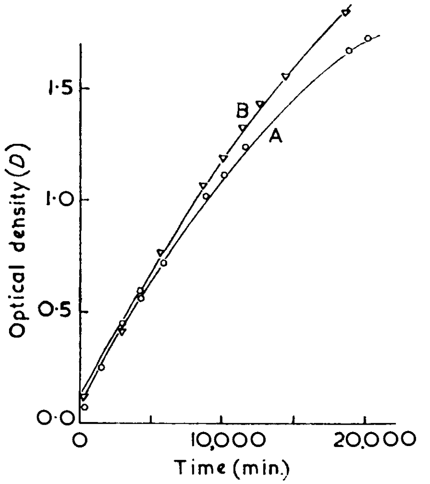

FIG. 6. Variation of optical density with time for a typical solution (0·057M) of 2,4,6-trinitrotoluene in pyridine at 25° (cell thickness 0·5 cm.).

A, At 440 mμ. B, At 510 mμ.

Pyridine solutions of 2,4,6-trinitrotoluene also show slow changes in conductivity and light absorption. Typical spectra are presented in Fig. 5. These solutions show a small initial conductivity κ_0 which varies with the square root of the concentration (c, in moles l.^{-1}) of the solute:

$$K_0 - K_{\text{py}} = 331 \times 10^{-8}c^{\frac{1}{2}} \text{ (at } 25^\circ\text{)}, \qquad (4)$$

where K_{py} is the specific conductivity of the solvent. Plots of optical density against time become almost linear after the first 800 min., the relation

$$\mathrm{d}D_{510}/\mathrm{d}t = 33{\cdot}2 \times 10^{-5}c^{\frac{1}{2}} \qquad (5)$$

being then obeyed at 25°. Changes in light absorption have been followed for periods of several weeks without attainment of equilibrium. Typical results are shown in Fig. 6.

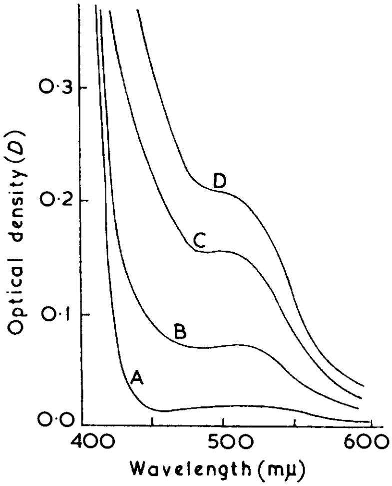

FIG. 7. Spectrum of a typical solution (0·049M) of 2,4,6-trinitro-*m*-xylene in pyridine (cell thickness 0·5 cm.).

Times after mixing: A, 30 min. B, 5500 min. C, 16,000 min. D, 26,000 min.

Pyridine solutions of 2,4,6-trinitro-*m*-xylene also show slow changes in conductivity and light absorption (see Fig. 7). Conductivity measurements for this system were not extensive but changes in light absorption were best fitted by the following relations at 25°:

$$10^6\mathrm{d}D_{510}/\mathrm{d}t = 4{\cdot}05c^{\frac{1}{2}} - 0{\cdot}14 \qquad (6)$$

and

$$10^4\mathrm{d}D_{440}/\mathrm{d}t = 3{\cdot}43c + 0{\cdot}005. \qquad (7)$$

Treatment of Results.—Measurements in benzene or ethanol show that *s*-trinitrobenzene forms a 1 : 1 complex with many amines or aromatic hydrocarbons and that the optical density at the wavelength at which the new band appears is directly proportional to the concentration of complex.[1] In the present case one of the reactants is the solvent and there seems good reason to suppose that only a small equilibrium concentration of primary product is formed. If a 1 : 1 complex were formed we should therefore expect $D''_{\text{eq.}}$ to be directly proportional to the initial *s*-trinitrobenzene concentration. Fig. 3 shows that this is not the case and $D''_{\text{eq.}}$ is more nearly a linear function of $c^{\frac{1}{2}}$, thus supporting the conductance measurements indicating ionisation. It appears therefore that in pyridine solutions of *s*-trinitrobenzene we have the following set of reactions:

$$\underset{(c-x)}{\mathrm{A}} + \underset{(b)}{\mathrm{B}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(x-y)}{{}^{-}\mathrm{A}\,.\,\mathrm{B}^+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{(y)}{\mathrm{A}^-} + \underset{(y)}{\mathrm{B}^+} \qquad (8)$$

where A and B are the acceptor and the donor, respectively, the various k's are velocity constants, and the concentrations are as shown ($b \approx b - x$).

The equilibria set up will be:

$$K_1 = [\mathrm{A}\,.\,\mathrm{B}]/[\mathrm{A}][\mathrm{B}] = (x - y)/[b(c - x)] \qquad (9)$$

and

$$K_2 = [\mathrm{A}^-][\mathrm{B}^+]/[\mathrm{A}\,.\,\mathrm{B}] = y^2/(x - y). \qquad (10)$$

There are three possibilities: (1) the complex A . B is responsible for the absorption at 570 mμ; (2) the ion A$^-$ is responsible for this absorption; and (3) both A$^-$ and AB absorb in this region. The third is the most reasonable and fits the results the best. Making this assumption we have

$$D = \varepsilon_1(x - y) + \varepsilon_2 y. \tag{11}$$

Combining this with eqns. (9) and (10) we have

$$D = \varepsilon_1 K_1 b(c - x) + \varepsilon_2(K_1K_2b)^{\frac{1}{2}}(c - x)^{\frac{1}{2}}. \tag{12}$$

We assume that the extinction coefficient is the same for the ion A$^-$ as for the complex, so that writing this common extinction coefficient as ε and assuming that $c \gg x$, we have

$$D/c^{\frac{1}{2}} = \varepsilon K_1 bc^{\frac{1}{2}} + \varepsilon(K_1K_2b)^{\frac{1}{2}}. \tag{13}$$

A plot $D/c^{\frac{1}{2}}$ against $c^{\frac{1}{2}}$ enables the values of K_1 and K_2 to be evaluated if a suitable value of ε can be assumed. Linear plots have been obtained at two temperatures and values of K_1 and K_2 estimated.

Treatment of the variation of D_{570} with time in terms of the above reaction scheme yields a complex expression. It has been simplified by a number of assumptions. In addition to those given above we assume that the rate-limiting step is the formation of the complex A . B and that dissociation occurs rapidly, so that A$^-$, B$^+$, and A . B are always in equilibrium with one another.

$$\mathrm{d}D/\mathrm{d}t = k_1b(c - x) - k_1(x - y). \tag{14}$$

By rearrangement, integration, combination with the equilibrium consideration outlined in equation (10), and introduction of the equilibrium concentrations of x and y (x_e and y_e respectively), we obtain:

$$-(k_{-1} + k_1b)t = \log_e\left\{(x_e - x) - P\left[Q - \left(\frac{K_2}{4} + x\right)^{\frac{1}{2}}\right]\right\} + \log_e(k_{-1} + k_1b)$$
$$+ \frac{P}{2(Q - P)}\log_e\frac{\left(\frac{K_2}{4} + x\right)^{\frac{1}{2}} - Q}{P + Q + \left(\frac{K_2}{4} + x\right)^{\frac{1}{2}}} + \text{Constant}, \tag{15}$$

where $P = K_2^{\frac{1}{2}}/(1 + K_1b)$ and $Q = [(K_2/4) + x_e]^{\frac{1}{2}}$. The integration constant may be evaluated from the fact that $x = 0$ when $t = 0$. Thus:

$$-(k_1 + k_1b)t = \log_e\frac{\left[(x_e - x) - P[Q - \left(\frac{K_2}{4} + x\right)^{\frac{1}{2}}\right]}{x_e - P\left[Q - \left(\frac{K_2}{4}\right)^{\frac{1}{2}}\right]}$$
$$+ \frac{P}{2(Q - P)}\log_e\frac{\left[\left(\frac{K_2}{4} + x\right)^{\frac{1}{2}} - Q\right]\left[P + Q + \left(\frac{K_2}{4}\right)^{\frac{1}{2}}\right]}{\left[P + Q + \left(\frac{K_2}{4} + x\right)^{\frac{1}{2}}\right]\left[\left(\frac{K_2}{4}\right)^{\frac{1}{2}} - Q\right]} \tag{16}$$

This expression has been used with our kinetic results and linear plots are obtained; it is a complex expression and to some extent depends on the accuracy of the equilibrium data obtained earlier, but the agreement is adequate. Plots of the right-hand side of eqn. (16) against time give ($k_{-1} + k_1b$) and from a knowledge of b and K_2 the two velocity constants can be calculated. Equilibrium and kinetic data obtained by these methods are shown in Table 1. In all cases it is assumed that ε = 10^4 l. mole^{-1} cm.$^{-1}$ and that it is independent of temperature.

TABLE 1.

	At 25°	At 39·7°		
K_1	8·0 × 10^{-5} l. mole^{-1}	4·2 × 10^{-5} l. mole^{-1}	$\Delta H°$	−8·2 kcal. mole^{-1}
K_2	4·1 × 10^{-4} mole l.$^{-1}$	1·3 × 10^{-4} mole l.$^{-1}$	$\Delta S°$	−46 e.u.
k_1	4·2 × 10^{-5} l. mole^{-1} min.$^{-1}$	4·5 × 10^{-5} l. mole^{-1} min.$^{-1}$	E_1	0·8 kcal. mole^{-1}
k_{-1}	0·5 min.$^{-1}$	1·1 min.$^{-1}$	$\Delta S_1^{\ddagger}$	−78 e.u.

DISCUSSION

Our results show that the *s*-trinitrobenzene–pyridine system is typical of the large group of aliphatic type complexes discussed earlier.[1] The primary spectrum at 465 and 570 mμ is typical of a complex which is essentially an ion pair A^-B^+ and ionises in a suitable environment. We assume that the extinction coefficient is the same for the free ion and for the complex, which is justified by Kolthoff, Stocesoca, and Lee's observation [4] that hydrogen-bond or ion-pair formation does not appreciably alter the absorption of visible light by the picrate ion in nitrobenzene.

A value of 10^4 l. mole^{-1} cm.$^{-1}$ has been assumed for ε since measurements on similar systems involving *s*-trinitrobenzene with aliphatic amines in ethanol indicate values close to this figure. The absolute value must remain doubtful since direct measurement in pyridine is impossible. Moreover, since K_1 is inversely proportional to ε the value of this quantity given above must be regarded as uncertain (it is probably within 50% of the true value). However, a reasonable variation makes little difference to $\Delta S°$ or $\Delta H°$ for complex formation. These are closely similar to those encountered in ethanol solution for aliphatic complexes and entirely different from those measured for the association of *s*-trinitrobenzene with a typical aromatic amine.[5] They are consistent with the formation of a salt-like product. The heat of formation is comparable with that found by Maryott [6] for tribenzylammonium picrate in benzene (−11·4 kcal. mole^{-1}), while the entropy of formation is comparable with that found for the Menschutkin reaction,[7] $Ph{\cdot}NMe_2 + MeI \longrightarrow Ph{\cdot}NMe_3{}^+I^-$.

It seems that the *s*-trinitrobenzene–pyridine complex is largely dissociated into ions in pyridine, whereas our measurements suggest that ionisation of the diethylamine–*s*-trinitrobenzene complex in ethanol occurs only to a small extent. This is surprising since ethanol is a more powerful ionising solvent than pyridine. A possible explanation is offered by Reid and Mulliken [8] who postulate the formation of the odd-electron ion $C_5H_5N{\cdot}^+$ in the pyridine–iodine system and suggest that it acquires stabilisation by resonance in pyridine solution. This would be brought about by combination of the ion with a pyridine molecule to form a structure analogous to that of biphenyl and involving a three-electron bond between two nitrogen atoms. No such stabilisation would be possible in ethanol solutions of diethylamine–*s*-trinitrobenzene.

The kinetic data fit equation (16) reasonably. Unfortunately errors inherent in the equilibrium data will be carried into the kinetic data through equation (16), so that the final results can be regarded as only approximate and have been included mainly to show that the data for reaction rates are compatible with those outlined in scheme (8). These results show a low activation energy and are consistent with the results in ethanol which indicated a value of the order of 5 kcal. mole^{-1}. Again the entropy of formation of the transition-state complex is large and negative, indicating an ordered structure for the transition state, which presumably involves solvent molecules.

Pyridine solutions of 2,4,6-trinitrotoluene and 2,4,6-trinitro-*m*-xylene show certain similarities to the pyridine–*s*-trinitrobenzene system, notably in the slow changes of light absorption and electrical conductivity. Exchange results show that proton-transfer reactions occur with both the methyl-substituted compounds. These systems presumably involve both of the reactions found with *s*-trinitrobenzene as well as proton transfer. The spectra are, however, so complex that we did not attempt to analyse the changes. Both systems show bands close to 510 mμ and the rate of change of D_{510} with time is in all cases proportional to the square root of the concentration of nitro-compound. The constant of proportionality decreases by a factor of about a hundred in passing from *s*-trinitrobenzene

---

[4] Kolthoff, Stocesoca, and Lee, *J. Amer. Chem. Soc.*, 1953, **75**, 1834.
[5] Bier, *Rec. Trav. chim.*, 1956, **75**, 866.
[6] Maryott, *J. Res. Nat. Bur. Stand.*, 1948, **41**, 7.
[7] Essex and Gelorimini, *J. Amer. Chem. Soc.*, 1926, **48**, 882.
[8] Reid and Mulliken, *J. Amer. Chem. Soc.*, 1954, **76**, 3869.

to 2,4,6-trinitrotoluene and again by a similar factor in passing from 2,4,6-trinitrotoluene to 2,4,6-trinitro-*m*-xylene, suggesting that a similar reaction is involved in each case.

It seems likely that the initial equilibria set up in 2,4,6-trinitrotoluene solutions are due to proton transfer. These solutions are initially purple and slowly become reddish-brown. Ainscough and Caldin [9] have reported that 2,4,6-trinitrotoluene undergoes two reactions with ethoxide ion which they formulate as a charge transfer and a proton transfer. It is the proton transfer which is the slower under their experimental conditions and they note that the solutions are at first brown, later becoming purple. This suggests that the relative rates of the two reactions are reversed in passing from ethanol at −80° to pyridine at room temperature. It seems that the proton transfer reaches equilibrium immediately and charge transfer then proceeds slowly as in the case of *s*-trinitrobenzene. Presumably a reaction analogous to the secondary reaction found in *s*-trinitrobenzene solutions also occurs.

Solutions of 2,4,6-trinitro-*m*-xylene are similar to those of 2,4,6-trinitrotoluene in this respect.

KING'S COLLEGE, NEWCASTLE UPON TYNE, 1.

[*Received, April 4th,* **1961.**]

---

[9] Ainscough and Caldin, *J.*, **1956**, 2546.