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CHEMICAL REACTIONS OF ELECTRON DONOR-ACCEPTOR SYSTEM: ON THE MECHANISM OF TRICYANOVINYLATION REACTION OF AROMATIC AMINES WITH TETRACYANOETHYLENE

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A new mechanism has been proposed for the tricyanovinylation reaction of aromatic amines with tetracyanoethylene.

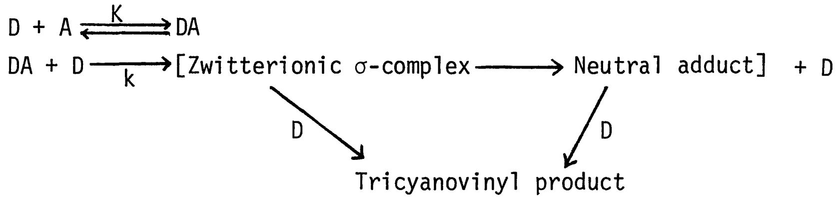
The mechanism of tricyanovinylation (TCV) reaction of aromatic amines with tetracyanoethylene (TCNE) has been the subject of recent numerous investigations.$^{1-9)}$ The TCV reaction is the most typical case involving the formation of charge-transfer (CT) complex, and the clarification of the reaction mechanism is very important in that it gives us a fundamental information as to the role of the CT-complex to the reaction which has been left ambiguously yet. In this communication we wish to point out that a currently accepted mechanism,$^{1-4)}$ in which a bimolecular exchange reaction between CT-complex and a donor molecule (D) is involved, is not an only possible mechanism, and wish to propose the possibility of another mechanism which can equally explain well the available kinetic data reported hitherto. In our new mechanism the bimolecular reaction between CT-complex and D is excluded, and instead a dissociation reaction of zwitterionic σ-complex back to the component molecule is involved as described in Scheme II or Scheme II'.

Background. In the TCV reactions in N,N-dimethylaniline-TCNE and indole-TCNE systems, which were investigated most extensively, it was found that 1:1 CT-complex formed between reactants gradually disappears to form the intermediate σ-complex or neutral adduct tetracyanoethane derivative (1st step of the reaction), and thereafter the final tricyanovinyl compound is slowly produced (2nd step of the reaction). These two steps of reactions could be followed independently by electronic absorption measurements because of the large difference in the reaction rates. In the first step the decay of the CT-complex followed the rate equation (I-1),

$$-\frac{d[DA]}{dt} = k_{obs}[DA] = \frac{kK[D]_{o}^{2}}{1 + K[D]_{o}}[DA] \qquad \text{(I-1)}$$

where DA, $[D]_o$, K, k_{obs} and k denote the CT-complex, initial concentration of D, association constant of CT-complex, pseudo first order rate coefficient of CT-complex and the rate coefficient for the process between CT-complex and σ-complex, respectively. This kinetic equation has to date been understood by a mechanism as described in Scheme I.

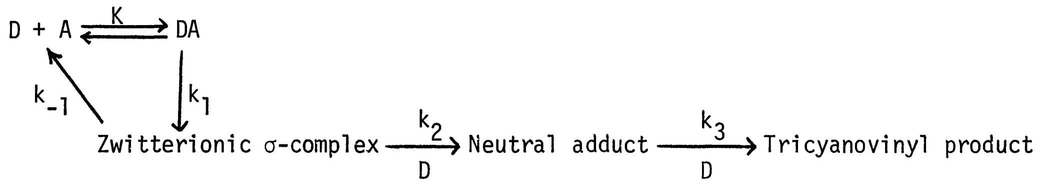
Scheme I



Introduction of a bimolecular reaction between CT-complex and D was postulated to be necessary in order to introduce $[D]_o^2$ term in the numerator of the rate equation (I-1).

New Mechanism. We wish now to propose another mechanism which can also satisfy all the kinetic data reported hitherto as described in Scheme II.[10)]

Scheme II



$$-\frac{d[DA]}{dt} = k_{obs}[DA] = \frac{k_1 k_2 K[D]_o^2}{(1 + K[D]_o)(k_{-1} + k_2[D]_o)}[DA] \qquad \text{(II-1)}$$

$$\approx \frac{(k_1 k_2/k_{-1})K[D]_o^2}{1 + K[D]_o}[DA] \qquad (k_{-1} \gg k_2[D]_o) \qquad \text{(II-2)}$$

The rate equation (II-1) reduces to (II-2) if $k_{-1} \gg k_2[D]_o$ holds, and (II-2) is essentially identical with (I-1), i.e., k in (I-1) is reinterpreted in the new mechanism as (k_1k_2/k_{-1}).

In this mechanism, an unstable zwitterionic σ-complex is assumed as an intermediate with the assumption of the reversibility of this compound back to the reactants. Mathematically, introduction of this back process from σ-complex to reactants makes $[D]_o$ term in the numerator of (II-1) and hence (II-2) quadratic.

So one can say that in the currently accepted mechanism the presence of DA + D reaction has been assumed in order to make the $[D]_o$ term in the numerator of k_{obs} quadratic, and in our new mechanism this is effected by introducing a back reaction from σ-complex to reactants.

Discussions. At present we have no further positive evidence to determine which of these mechanisms is correct. However, we believe that the new mechanism is more reasonable from the following reasons.

(1) The reaction of complexed TCNE with a free donor, the currently accepted mechanism, is difficult to understand in such an electrophilic substitution reaction as TCV reaction because the electron accepting property of the complexed TCNE is sufficiently weakened. Furthermore, no experimental evidence has been found which shows the existence of the exchange reaction between a complexed donor and a free donor.

(2) The kinetic studies for the 2+2 and 4+2 cycloaddition reactions of electron-donating olefins with TCNE has revealed that the reaction should be understood as either unimolecular transformation of the CT-complex or bimolecular reaction between free donor and acceptor molecules.[11),12)] This result suggests that the unimolecular transformation of the CT-complex is favored over bimolecular reaction between the CT-complex and a free donor. Thus, the primary process of the chemical reaction involving the formation of the CT-complex is systematically understood by the same mechanism both for the TCV reaction and the cycloaddition reaction.

(3) The assumption of back process of the zwitterionic σ-complex to component molecules is reasonable, which has recently been evidenced in the 2+2 cycloaddition reaction of isomeric enol ethers with TCNE.[13)]

(4) The new mechanism which involves σ-complex as an unstable intermediate and neutral adduct tetracyanoethane derivative as an accumulating intermediate is in accord with the fact that the latter has actually been isolated,[6,9,14)] while the former can not be detected even by the spectroscopic method. The

explanation in the literature that the isolable neutral adduct may arise by rapid rearrangement of the σ-complex and may not be on the reaction path of the overall TCV reaction under the kinetic work conditions seems to be unattractive.

Comments. (1) As shown in Scheme II, the unimolecular transformation of the CT-complex is proposed and the CT-complex is assumed as a true intermediate, but another mechanism is possible in which σ-complex is produced from the component molecules and the CT-complex exists in a side reaction as shown in Scheme II'. The reaction scheme and rate equation are as follows,[10)]

Scheme II'

$$\begin{tikzcd} D + A \arrow[r, shift left, "K"] \arrow[d, shift left, "k_1'"] & DA \arrow[l, shift left] & \\ \text{Zwitterionic } \sigma\text{-complex} \arrow[u, shift left, "k_{-1}"] \arrow[r, "k_2", "D"'] & \text{Neutral adduct} \arrow[r, "k_3", "D"'] & \text{Tricyanovinyl product} \end{tikzcd}$$

$$-\frac{d[DA]}{dt} = k_{obs}[DA] = \frac{k_1'k_2[D]_\circ^2}{(1 + K[D]_\circ)(k_{-1} + k_2[D]_\circ)}[DA] \qquad \text{(II'-1)}$$

$$\approx \frac{(k_1'k_2/k_{-1}K)K[D]_\circ^2}{1 + K[D]_\circ}[DA] \qquad (k_{-1} \gg k_2[D]_\circ) \qquad \text{(II'-2)}$$

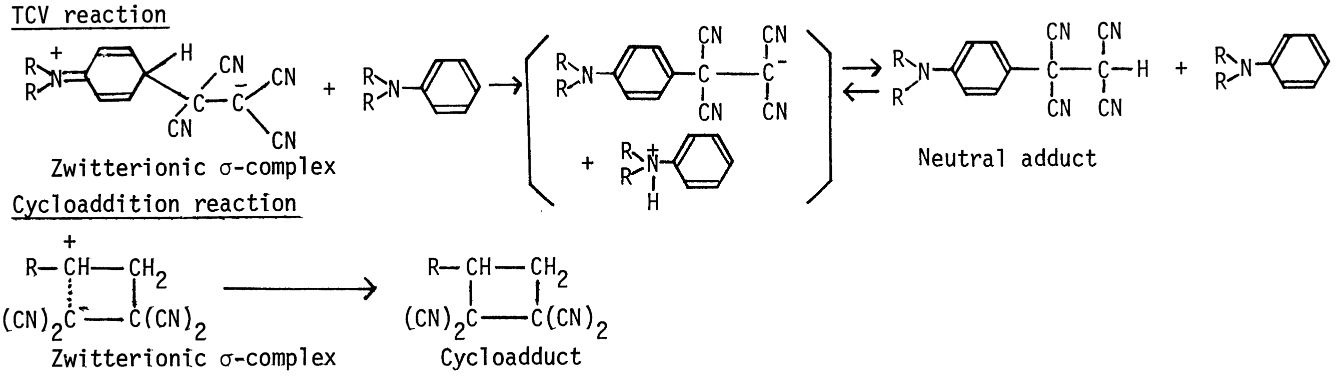
$$k_1' = k_1K \qquad \text{(II'-3)}$$

where k_1' is the rate coefficient from the component molecules to the σ-complex. The two mechanisms, Scheme II and Scheme II', can not be differentiated kinetically since the relationship described in equation (II'-3) always holds.[11),12)]

(2) The kinetic data for the aniline-TCNE system[5)] where TCV occurs at the nitrogen atom has showed that the pseudo first order rate constant of the CT-complex, k_{obs}, can be given by $kK[D]_\circ^3/(1 + K[D]_\circ)$. This cubic dependence of $[D]_\circ$ in the numerator of k_{obs} is interpreted in our mechanism in terms of the reversibility of both processes of σ-complex and neutral adduct formations[15)] probably due to the instability of neutral adduct in this system, being consistent with the fact that the absorption band of neutral adduct could not be detected by electronic absorption spectra only in this system.

(3) The apparent difference in the rate equation for the decay of the CT-complex between the TCV reaction and the cycloaddition reaction is understandable as resulting from the fact that in the TCV reaction one more donor molecule participates in abstracting a proton from the σ-complex in the neutral adduct formation process, while in the cycloaddition reaction such a process is not involved (Scheme III).

Scheme III



(4) It has to date been insisted that the CT-complex is the essential intermediate in the TCV reaction based on the mechanism of the bimolecular reaction of the complexed donor and a free donor, however, in the new mechanism the kinetic data alone can not tell whether or not the CT-complex is the true intermediate in the TCV reaction as well as in the cycloaddition reaction.

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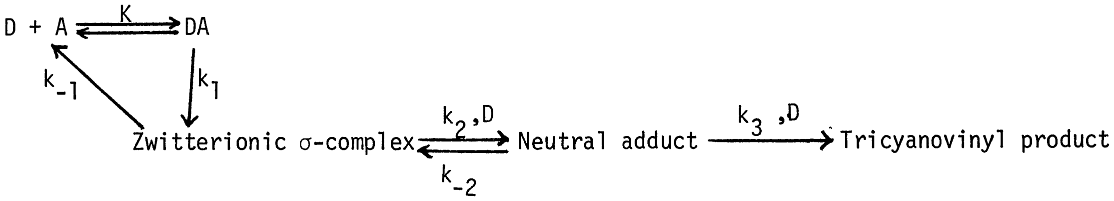
14) The isolable neutral adduct tetracyanoethane derivative might exist as a carbanion species (see Scheme III) in a solution.
15) The reaction scheme and rate equation of aniline-TCNE system in which the neutral adduct formation process is reversible are given as follows (Scheme IV).

Scheme IV



$$-\frac{d[DA]}{dt} = k_{obs}[DA] = \frac{k_1k_2k_3K[D]_\circ^3}{(1 + K[D]_\circ)(k_{-1}k_{-2} + k_{-1}k_3[D]_\circ + k_2k_3[D]_\circ^2)}[DA] \qquad (IV\text{-}1)$$

$$\approx \frac{(k_1k_2k_3/k_{-1}k_{-2})K[D]_\circ^3}{1 + K[D]_\circ}[DA] \qquad (k_{-1}/k_2 >> [D]_\circ,\ \text{and}\ k_{-2}/k_3 >> [D]_\circ) \qquad (IV\text{-}2)$$

The rate equation (IV-1) is derived by applying steady-state approximations to the σ-complex and neutral adduct. The equation (IV-1) reduces to (IV-2), which has a $[D]_\circ^3$ dependence in the numerator of k_{obs}, if $k_{-1}/k_2 >> [D]_\circ$ and $k_{-2}/k_3 >> [D]_\circ$ hold. Another mechanism is also possible in which the σ-complex is produced from the component molecules.

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