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QUATERNARY AMMONIUM SALTS AS A QUASI-STABLE INTERMEDIATE IN TRIETHYLENEDIAMINE-CATALYZED AMINOLYSIS OF PHENYL N-PHENYLCARBAMATES WITH ANILINE

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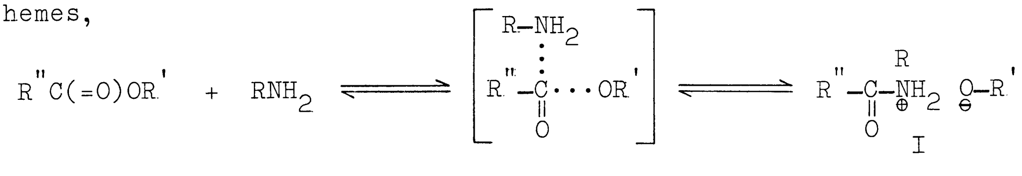
An identification of quaternary ammonium salts formed as a quasi-stable intermediate in the course of the triethylenediamine-catalyzed aminolysis of phenyl N-phenylcarbamates with aniline was performed by UV spectroscopic measurements and semiempirical ASMO-SCF calculations.

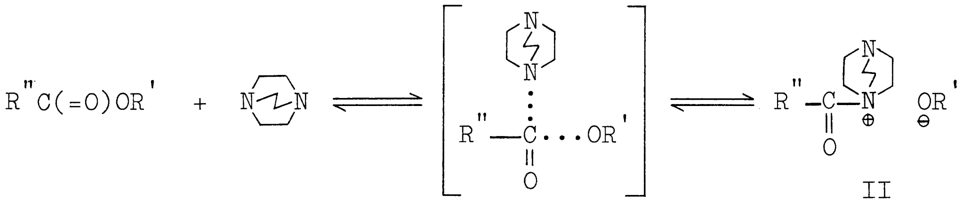
Although some quantitative studies of the kinetics of aminolysis or amidation reaction have been recorded, the successful interpretation of the reaction mechanism from the viewpoint of molecular level is still in an early stage. The mechanism is at present in a tangle due to the following three distinctive proposals: (a) base (or base-acid) catalysis,[1-4] (b) concerted mechanism,[5,6] and (c) mechanism involving a quasi-stable intermediate of quaternary ammonium salts.[7,8] Our proposal c is represented by the following schemes,



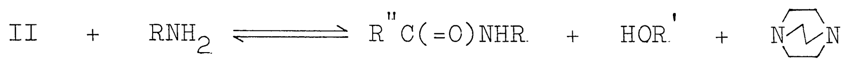
(1)

$$\mathrm{I} \longrightarrow R''C(=O)NHR + HOR' \qquad (2)$$

or, in the presence of such a catalyst as triethylenediamine (TED),



(3)



$$\text{II} + \text{RNH}_2 \rightleftharpoons \text{R}''\text{C(=O)NHR} + \text{HOR}' + \text{N}\langle\rangle\text{N} \qquad (4)$$

Now, the identification of an intermediacy of quaternary ammonium salt denoted as I and/or II seems to be significant and urgent.

In this paper, the results of UV spectroscopic and theoretical studies are presented, which were undertaken to elucidate the mechanism of the TED-catalyzed aminolysis of phenyl or p-chlorophenyl N-phenylcarbamate (PPC or CPC respectively) with aniline in dioxane.

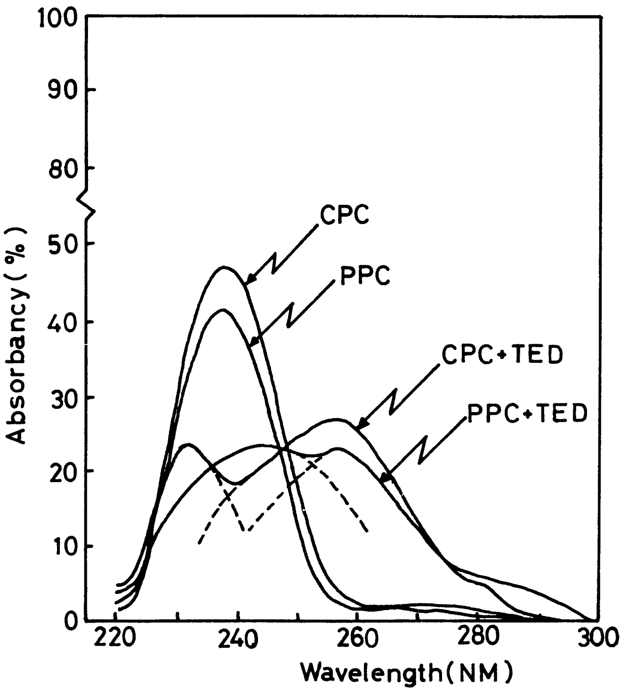


Fig. 1. UV spectra of PPC and CPC in the presence or absence of TED (in dioxane).

Let us discuss first the absorption spectra of PPC and/or CPC in the presence or absence of TED. It is noticeable from Fig. 1 that the couple of PPC-TED and of CPC-TED, which were preheated without aniline at 80°C for 3 hr in dioxane, indicates new absorption bands: λ_{max} = 245 and 256 nm for the former; 232 and 256.5 nm for the latter. The new bands do not accord with those of original compounds (PPC and CPC) and phenyl isocyanate (λ_{max} = 242.5 nm in dioxane).

Some remarks should be here made of the interaction between PPC (and/or CPC) and TED: bearing in mind that the HOMO of the latter and the LUMO of the former are strongly localized in the nonbonding lone-pair N-orbital (MO: −10.29 eV; AO population: 1.917) and the nonbonding vacant-like C-orbital of central carbonyl carbon (MO: −7.96 eV for PPC and −7.93 eV for CPC; AO population: 0.588 for the both) respectively, it is sure from some kinetic evidences that the aminolysis reaction proceeds via the transition state shown in Eq. (3).$^{9)}$

Next, let us interpret the electronic excitations of the new absorption bands. The excitation energies of quaternary ammonium salts (I and II) were then calculated by a semiempirical ASMO-SCF method;$^{10)}$ For the simplicity of computations,

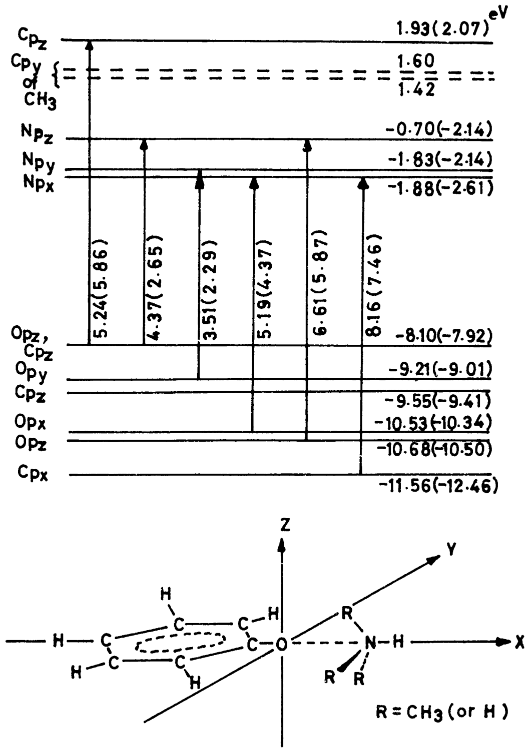


Fig. 2. A diagram for main transition energies of $H(CH_3)_3\overset{\oplus}{N}\overset{\ominus}{O}C_6H_5$ and $H_4\overset{\oplus}{N}\overset{\ominus}{O}C_6H_5$ in their ionic structure ($\overset{\oplus}{N}\cdots\overset{\ominus}{O} = 3.2$ Å). Values in parentheses are those obtained from the ASMO-SCF calculations on $H_4\overset{\oplus}{N}\overset{\ominus}{O}C_6H_5$.

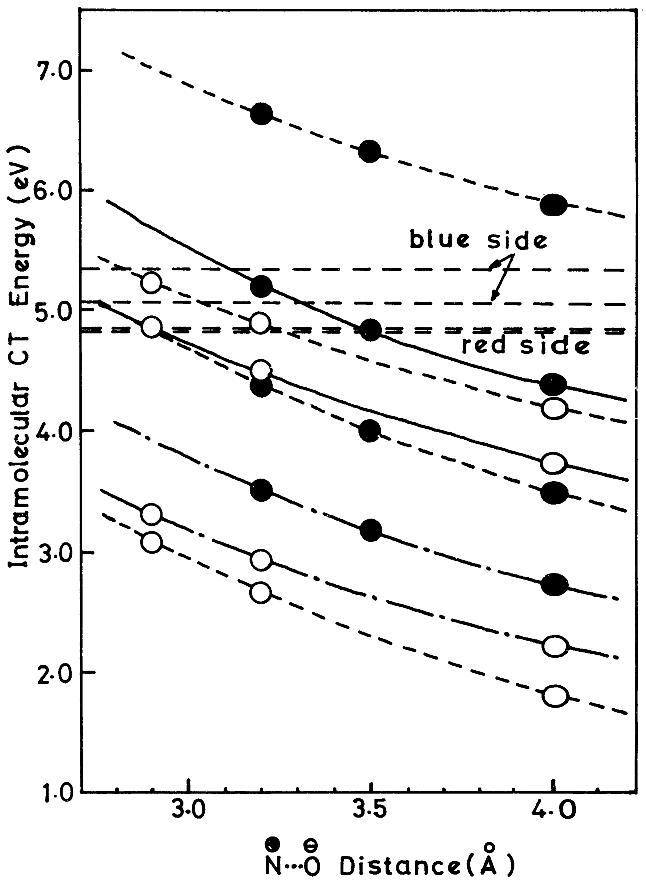


Fig. 3. Intramolecular CT energy vs. $\overset{\oplus}{N}\cdots\overset{\ominus}{O}$ distance.

○: $H_4\overset{\oplus}{N}\ \overset{\ominus}{O}C_6H_5$; ●: $H(CH_3)_3\overset{\oplus}{N}\ \overset{\ominus}{O}C_6H_5$

——: $(O_{p_x})^2 \longrightarrow (O_{p_x})(N_{p_x})$

–·–: $(O_{p_y})^2 \longrightarrow (O_{p_y})(N_{p_y})$

– – –: $(O_{p_z})^2 \longrightarrow (O_{p_z})(N_{p_z})$

the ASMO-SCF calculations were performed on two model ammonium salts simulated as $H_4\overset{\oplus}{N}\overset{\ominus}{O}C_6H_5$ and $H(CH_3)_3\overset{\oplus}{N}\overset{\ominus}{O}C_6H_5$, with variation in the distance of $\overset{\oplus}{N}\cdots\overset{\ominus}{O}$ in the range of values from the purely covalent ($\overset{\oplus}{N}\cdots\overset{\ominus}{O} = 2.9$ Å) to a van der Waals distance ($\overset{\oplus}{N}\cdots\overset{\ominus}{O} = 4.0$ Å).

In Fig. 2 is presented a diagram for the main singlet excitation energies of $H(CH_3)_3\overset{\oplus}{N}\overset{\ominus}{O}C_6H_5$ and $H_4\overset{\oplus}{N}\overset{\ominus}{O}C_6H_5$; A couple of new bands (red side = 4.82~4.86 eV and blue side = 5.06~5.35 eV in Fig. 1) are directly related to the transitions of electrons between the central nitrogen of cation part and the oxygen of counteranion part; TED itself stays in its ground state under the UV range of 320～200 nm. Taking notice of the changes in above-mentioned excitation energies due to the stretching of the $\overset{\oplus}{N}\cdots\overset{\ominus}{O}$ distance (see Fig. 3), the red side transition is assigned to the intramolecular CT $[(O_{p_x})^2 \longrightarrow (O_{p_x})(N_{p_x})]$11) and the blue side one includes the other intramolecular CT transitions such as $[(O_{p_z})^2 \longrightarrow (O_{p_z})(N_{p_z})]$.

In conclusion, the aminolysis reaction of ester with amine proceeds via a quasi-stable intermediate of quaternary ammonium salt, I or II. The aminolysis in lower molecules will indicate surely the intramolecular CT spectra belonging to the quaternary ammonium salt, which will be published in the near future.

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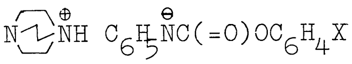
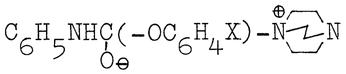
9) The decrease in the bond population of C-O single bond in PPC (from 0.712 to 0.554) caused by the long-range nucleophilic interaction of TED ($N\cdots C > 2.0$ Å) suggests the weakening of the C-O. It is hardly expected from the results of calculations that such ammonium-type salts as  $N\overset{\oplus}{N}H\ C_6H_5\overset{\ominus}{N}C(=O)OC_6H_4X$ and  $C_6H_5NH\underset{O^{\ominus}}{C}(-OC_6H_4X)-\overset{\oplus}{N}N$ (X = H or Cl) are formed in the reaction of PPC (or CPC) and TED.

10) With regard to the details of calculation method, see K. Ohkubo and H. Kanaeda, Trans. Faraday Soc., 68, 1164 (1972).

11) Notations of O_{p_x}, N_{p_x}, C_{p_x}, etc. indicate the p_x-orbitals of O, N, and C (in benzene ring), etc., respectively. Each molecular orbital is strongly occupied by the above-mentioned AO.

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