RELATION BETWEEN CHEMICAL STRUCTURE OF o-CARBOXYAMIDES AND THEIR REACTIVITY IN INTRAMOLECULAR DECOMPOSITION REACTION

O. A. Mukhina, P. P. Nechaev,
V. A. Kosobutskii, and Ya. S. Vygodskii

UDC 541.127:530.145:542.92:547.584

The intramolecular decomposition of compounds that contain a carboxyl group ortho to the amide linkage has great practical importance for the synthesis of heat stable polymers, the polyimides [1]. Consequently, for predicting the reactivity of these compounds it is important to establish a detailed mechanism for the decomposition of o-carboxyamides and find the relation between their reactivity and the chemical structure.

When the literature data on this problem are analyzed, it can be observed that the rate of the reaction for the intramolecular decomposition of o-carboxyamides is strongly dependent on their structure [2-7]. Thus, for example, when the H atoms are replaced by methyl groups in the anhydride component of malamic acids the intramolecular decomposition rate constant increases by $\sim 10^4$ times [2, 3].

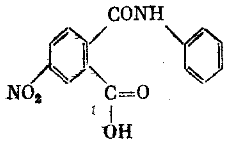
Various authors propose various approaches for ascertaining the quantitative rules for the relation between the reactivity of o-carboxyamides and the chemical structure. A series of N-aryl-substituted malanilic and phthalanilic acids was studied in [3, 4] and a linear relation was obtained between the intramolecular decomposition rate constants and the pK_a of the formed amine [4], as well as correlation with the Hammett σ constants [5]. However, similar correlations are not observed in the hydrolysis of the N-alkyl-substituted malamic and phthalamic acids [3, 6]. Besides this, such relations [2, 3] do not permit comparing the reactivity of o-carboxyamides with substituents in the anhydride component.

In our opinion, the approach proposed in [7] is more general, since it is based on the fact that the quantum chemical calculations take into account the effect of substituents in both the amine and anhydride components on the relative distribution of the electron density in the molecule. To verify this assumption we studied the rate for the intramolecular decomposition of 4-nitrophthalanilic acid.

EXPERIMENTAL

4-Nitrophthalanilic acid was synthesized from 4-nitrophthalic anhydride and aniline in chloroform at ~20°C.

The quantum-chemical calculations were run within the framework of the semiempirical CNO method as described in [7]. The calculations disclosed that the following isomer is energetically more favorable:



The pH value of 0-2 needed for the aqueous solutions was obtained by using HCl and standard buffer mixtures.

The intramolecular decomposition rate of 4-nitrophthalanilic acid was studied spectrophotometrically [7], on the basis of the accumulation of aniline (λ 440 nm) and consumption of 4-nitrophthalanilic acid (λ 290 nm). The effective rate constants were calculated using the first-order equation.

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. All-Union Scientific-Research Institute of Synthetic Resins, Vladimir. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1640-1642, July, 1979. Original article submitted December 25, 1978.

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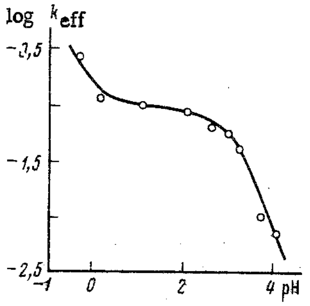


Fig. 1

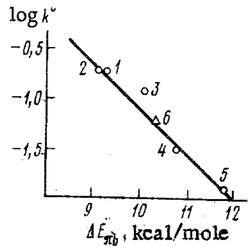


Fig. 2

Fig. 1. Dependence of log k_{eff} (min^{-1}) for intramolecular decomposition of 4-nitrophthalanilic acid on pH of aqueous solutions (50°C).

Fig. 2. Dependence of log k^0 (min^{-1}) on $\Delta E_{\pi b}$ (kcal/mole) for intramolecular decomposition of phthalanilic acids of variable structure. 1) X = OH; 2) CH_3; 3) H; 4) COOH; 5) NO_2; 6) Y = NO_2.

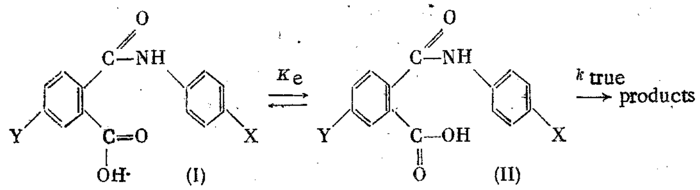
DISCUSSION OF RESULTS

The experimental data on the intramolecular decomposition of 4-nitrophthalanilic acid are plotted in Fig. 1. They are described well by the following equation:

$$k_{eff} = k^0_{true}/(1 + K_{diss}/h_a)$$

The calculated values are $k^0_{true} = 8.7 \cdot 10^{-2}$ min^{-1}, $K_{diss} = 6.92 \cdot 10^{-4}$.

On the basis of the kinetic data and quantum-chemical calculations, the following mechanism was proposed in [7] for the intramolecular decomposition of o-carboxyamides:



Taking into account the fact that the order of reactivity obtained in [7] is the reverse of that obtained in the hydrolysis of N-phenyl-substituted anilides [8, 9], it was postulated that the limiting step is not the decomposition of the amide linkage, but rather the formation of isomer (II). In harmony with this, we obtained the linear function: k^0_{true} vs $\Delta E_{\pi b}$, the difference in the states of isomers (I) and (II).

The appropriate quantum-chemical calculations were made for 4-nitrophthalanilic acid, and the quantity $\Delta E_{\pi b} = 10.34$ kcal/mole. From Fig. 2 it can be seen that the rate constant for the intramolecular decomposition of 4-nitrophthalanilic acid correlates well with this value.

As a result, it can be said that this approach makes it possible to predict the reactivity of o-carboxyamides with various substituents in both the anhydride and amine components.

CONCLUSIONS

1. A study was made of the intramolecular decomposition rate of 4-nitrophthalanilic acid and quantum-chemical calculations of the molecule were made within the framework of the semiempirical CNO method.

2. A comparison of the kinetic data and the results of the quantum-chemical calculations makes it possible to predict the reactivity of o-carboxyamides of variable structure.

LITERATURE CITED

1. E. V. Kamzolkina, P. P. Nechaev, V. S. Markin, Ya. S. Vygodskii, T. V. Grigor'eva, and G. E. Zaikov, Dokl. Akad. Nauk SSSR, 219, 138 (1974).

2. A. J. Kirby and P. W. Lancaster, J. Chem. Soc. Perkin Trans. 2, 1206 (1972).
3. M. F. Aldersley, A. J. Kirby, P. W. Lancaster, R. S. McDonald, and C. R. Smith, J. Chem. Soc. Perkin Trans. 2, 1487 (1974).
4. R. Klyger and C. H. Lam, J. Am. Chem. Soc., 97, 5536 (1975).
5. M. D. Hawkins, J. Chem. Soc. Perkin Trans. 2, 642 (1976).
6. J. Dahlgren and N. L. Simmerman, J. Phys. Chem., 69, No. 10, 3626 (1965).
7. P. P. Nechaev, O. A. Mukhina, V. A. Kosobutskii, V. K. Belyakov, Ya. S. Vygodskii, Yu. V. Moiseev, and G. E. Zaikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1750 (1977).
8. C. J. Giffney and C. J. O'Connor, J. Chem. Soc. Perkin Trans. 2, 1357 (1975).
9. J. Kovalek and V. Sterba, Collect. Czech. Chem. Commun., 40, 1924 (1975).

PRODUCTS AND PHOTOCHEMICAL DECOMPOSITION RATE OF CYCLOHEXANESULFONYL CHLORIDE IN PRESENCE OF OXYGEN

M. A. Saitova and R. F. Khalimov

UDC 541.127:541.141:542.92:547.541.51

The hypothesis given in [1] that the sulfonic peracid (RSO_4H) is formed as the primary molecular product in the chain sulfooxidation of saturated hydrocarbons, the subsequent transformations of which lead to the formation of the end reaction product, the sulfonic acid (RSO_3H), has found wide acceptance, although experimental data that support it are practically lacking.

We studied the sequence of forming the indicated products on the example of the photoinitiated decomposition of cyclohexanesulfonyl chloride (RSO_2Cl) in cyclohexane (RH) in the presence of O_2.

EXPERIMENTAL

The experiments were run in a thermostatted quartz reactor at $[RSO_2Cl] = 1$ mole / liter, the volume of the reaction mixture was 20 ml, and the O_2 feed rate was 6 liters / h. The bubbling conditions of the reaction assured the accumulation of the necessary concentration of the reaction products and the removal of HCl from the reaction mixture. The O_2 absorption was followed using a manometric assembly with automatic stabilization of the pressure [2]. It was established that at a partial O_2 pressure of $pO_2 \geq 100$ mm of Hg in the O_2-Ar gas mixture the O_2 absorption rate is independent of pO_2 and the rate of stirring the reaction mixture. The experiments were run at $pO_2 = 760$ mm. The light source was a DRT-200 lamp without a light filter. The RSO_2Cl was analyzed polarographically [3]. The total amount of RSO_4H and RSO_3H was determined by potentiometric titration [4]. The RSO_4H was determined iodometrically [5]. The RSO_3H concentration was calculated from the difference in the results of these analyses. The HCl was determined by the Volhard method [6], and the amount of water was determined by the Fischer method [5]. The cyclohexanol (ROH) and cyclohexanone (R'O) were analyzed by GLC [7]. The RSO_2Cl was obtained by the photochemical sulfochlorination of RH [8]. The RH was freed of impurities by treating it repeatedly with a 10% solution of oleum in H_2SO_4 and subsequent distillation.

DISCUSSION OF RESULTS

The photoinitiated decomposition of RSO_2Cl in the presence of O_2 gives RSO_3H, H_2O, HCl, ROH, R'O, and also a hydroperoxide, which exhibits acid properties and titrates along with the RSO_3H. We identified this hydroperoxide to be RSO_4H, since reduction of the hydroperoxide with KI, and also its thermal decomposition, lead to RSO_3H. The crystallohydrate $C_6H_{11}SO_3H \cdot H_2O$ was isolated from the reaction products, which was characterized by the IR spectrum: SO_2 (1100-1250 cm^{-1}), S=O (1045 cm^{-1}), C−S (700-800 cm^{-1}), and by elemental analysis. Found: C 39.0; H 7.5; S 17.2%. $C_6H_{14}SO_4$. Calculated: C 39.5; H 7.7; S 17.6%.

Institute of Chemistry, Bashkir Branch of the Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1642-1644, July, 1979. Original article submitted December 27, 1978.

0568-5230/79/2807-1518$07.50