THERMAL DECOMPOSITION OF ACYL NITRATES

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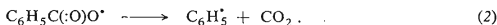
Main products of the thermal decomposition of benzoyl nitrate, *p*-toluyl nitrate and *p*-nitrobenzoyl nitrate in tetrachloromethane and acetonitrile solutions were determined quantitatively. The data thus obtained were used to discuss the effect of the substituent in acyl nitrate and the effect of the solvent on chemical transformations and reactions of free radicals arising during the thermal decomposition of acyl nitrates.

Barlow[1] identified, by using infrared spectroscopy and GLC, the main products of the thermal decomposition of benzoyl nitrate in mixtures of tetrachloromethane with benzene and of tetrachloromethane with toluene. The products were benzoic acid, its anhydride, nitrobenzene, *m*-dinitrobenzene, phenyl benzoate, and diphenyl. On the basis of their character he assumes radical decomposition of benzoyl nitrate

$$C_6H_5C(:O)ONO_2 \longrightarrow C_6H_5C(:O)O^\bullet + NO_2 \qquad (1)$$
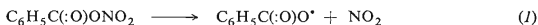
and decarboxylation of the benzoyloxy radicals

$$C_6H_5C(:O)O^\bullet \longrightarrow C_6H_5^\bullet + CO_2 . \qquad (2)$$

Since a tetrachloromethane–benzene mixture was used as solvent, it was not possible to estimate whether nitrobenzene is formed by nitration of benzene with nitrogen pentoxide released from benzoyl nitrate[2-4] by the reaction

$$2 C_6H_5C(:O)ONO_2 \rightleftharpoons N_2O_5 + (C_6H_5CO)_2O \qquad (3)$$
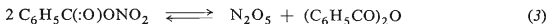
or also by a reaction of phenyl radicals with nitrogen dioxide or benzoyl nitrate as in the radical decomposition of benzoyl hypochlorite[5-7]. The amount of carbon dioxide released during the thermal decomposition of benzoyl nitrate was not determined either. The data published on this decomposition process[1-4] are qualitative as a rule and do not give any idea about the relations between its partial reactions.

In order to elucidate the mechanism of thermal decomposition of acyl nitrates we determined the amount of the main products of decomposition of benzoyl nitrate, *p*-toluyl nitrate and *p*-nitrobenzoyl nitrate in boiling tetrachloromethane and acetonitrile.

The resulting compounds identified by us and their respective amounts are given in Table I. The formation of carbon dioxide and carboxylic group is in accordance

with the earlier assumed[1] radical mechanism of the decomposition of acyl nitrate according to Eqs (1) and (2). In tetrachloromethane solution, in which the acyloxyl radical can remove the hydrogen atom only from the original acyl nitrate and its decomposition products, the greater part of the carboxyl radicals was decarboxylated, while the smaller part was transformed into a carboxylic acid. The amount of the acid $XC(:O)OH$ in tetrachloromethane is highest in the case of p-toluyl nitrate, which may be ascribed to the greater reactivity of the acyloxyl radical towards the methyl group on the aromatic ring than towards the ring itself[8]. The amount of carbon dioxide detected in acetonitrile solution was lower than that in tetrachloromethane solution. This fact, along with the transformation of 70% of p-nitrobenzoyl nitrate into p-nitrobenzoic acid in acetonitrile solution indicates that the benzoyloxyl radicals react with acetonitrile. It cannot be estimated, however, whether the benzoyloxyl radicals do not react with tetrachloromethane, and consequently become prevailingly decarboxylated, or whether they react with it with formation of acyl hypochlorite, which then decomposes to yield carbon dioxide and arylhalogen[7,9].

The sum of amounts of carbon dioxide and of the acid $XC(:O)OH$ corresponding to the decomposition of one mol of $XC(:O)ONO_2$ varies from 0·66 to 0·98 mol (Table I). The missing part of the $C(:O)O-$ group is probably contained in the anhydride $(XCO)_2O$, which was detected in the mixtures by gas chromatography and mass spectrometry, and in a number of acids and esters obtained by combination of the $\dot{X}C(:O)OH$ radicals (where $\dot{X}$ is the residue after removal of the atom H from X), and of $XC(:O)\dot{O}$ with other radicals, for instance with X, $\dot{X}Cl$, $\dot{X}NO_2$, $\dot{C}Cl_3$,

TABLE I

Main Products of Thermal Decomposition of Acyl Nitrates $XC(:O)ONO_2$

X	t h	Products, mol/mol nitrate				
		CO_2	$XC(:O)OH$	XNO_2	XCl	XCN
Decomposition in CCl_4 (76°C)[a]						
C_6H_5	9[b]	0·65	0·12	0·06	0·32	—
p-$CH_3C_6H_4$	14[c]	0·61	0·31	0·07	0·15	—
p-$O_2NC_6H_4$	9	0·59	0·18	0·03	0·03	—
Decomposition in CH_3CN (81°C)[a]						
p-$CH_3C_6H_4$	14	0·33	0·33	0·11	—	0·08
p-$O_2NC_6H_4$	5	0·28	0·70	0·015	—	0·01

[a] The presence of XH was proved qualitatively each time. [b] The presence of $(C_6H_5CO)_2O$ was proved qualitatively. [c] 0·025 mol of $(p$-$CH_3C_4H_4CO)_2O$/mol nitrate also detected.

and $\dot{N}O_2$. In accordance with the above assumption, the decomposition of acyl nitrates in acetonitrile gave rise to *p*-toluylic acid, which by reacting with radicals comparatively readily yields $\dot{C}H_2C_6H_4CO(:O)OH$. The amount of *p*-toluylic acid obtained was much lower than that of *p*-nitrobenzoic acid. In the decomposition products of benzoyl nitrate gas chromatography and mass spectrometry revealed the presence of phenyl benzoate.

The diversity of interactions of the radical intermediates is also corroborated by gas chromatograms of the reaction mixtures in which one can see a great number of compounds in insignificant concentrations (Fig. 1). To the formation of these compounds not only the primary acyloxyl radicals, but also the phenyl, *p*-methylphenyl and *p*-nitrophenyl radicals contribute due to the decarboxylation of the primary radicals. The products of combination of secondary radicals include compounds XNO_2 (Table I) and a small amount of diphenyl proved by gas chromatography and mass spectrometry in the decomposition products of benzoyl nitrate. The reaction products of secondary radicals with solvents are exemplified by compounds XCl, XCN, and XH (Table I). *p*-Tolunitrile and *p*-nitrobenzonitrile were isolated from the products of the thermal decomposition of *p*-toluyl nitrate and *p*-nitrobenzoyl nitrate in acetonitrile solution by gas chromatography and identified by mass spectroscopy. Their presence in the reaction mixture suggests that the *p*-methylphenyl and *p*-nitrophenyl radicals remove from the acetonitrile molecule not only a hydrogen atom, but also the CN group.

In the mixture of 10 ml of the solution of *p*-toluyl nitrate in acetonitrile (0.2 mol/1) with 20 ml of benzene, nitrobenzene was determined chromatographically after boiling for seven hours in an amount of 0.07 mol per 1 mol of the initial *p*-toluyl
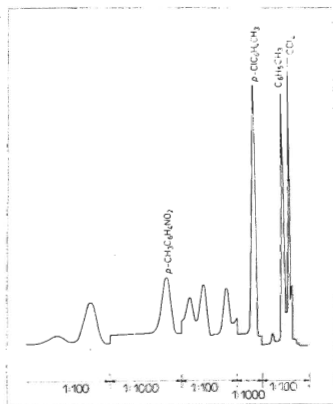

FIG. 1

Chromatogram of Products of Thermal Decomposition of *p*-Toluyl Nitrates in Tetrachloromethane at 76°C

nitrate. Its amount is comparable with that of *p*-nitrotoluene and *p*-tolunitrile arising during the thermal decomposition of *p*-toluyl nitrate in pure acetonitrile (Table I) by a reaction of the *p*-methylphenyl radical with nitrogen dioxide and acetonitrile. The formation of nitrobenzene in the thermal decomposition of *p*-toluyl nitrate in the presence of benzene may therefore be explained by the transfer of the *p*-toluyloxyl and *p*-methylphenyl radicals to benzene followed by the reaction of the phenyl radicals thus obtained with nitrogen dioxide. Although the parallel nitration of benzene with nitrogen dioxide[3] arising in the reaction mixture according to Eq. (3) cannot be ruled out in this case, it may be inferred that this reaction does not participate in the formation of nitrobenzene to an extent not considerably greater than the reaction of the phenyl radical with nitrogen dioxide. The total participation of the X groups in the decomposition products determined here varies from 0·47 to 0·73 mols per 1 mol of the initial nitrate (Table I). The rest is scattered in a large number of other products of numerous radical reactions.

EXPERIMENTAL

Initial Compounds

Benzoyl chloride, b.p. 78°C/10 Torr, *p*-toluyl chloride, b.p. 105°C/15 Torr, *p*-nitrobenzoyl chloride, m.p. 75°C. Silver nitrate, reagent grade, was remelted and after pulverization stored in an evacuated desiccator over phosphorus pentoxide. Tetrachloromethane, reagent grade, and acetonitrile for spectroscopic measurements were dried over phosphorus pentoxide and redistilled in a stream of dry nitrogen. Solutions of acyl nitrates were prepared by a modified procedure after Francis[10] by mixing solutions of acyl chloride and silver nitrate in a given solvent at −15°C, stirring the mixture at the same temperature for two hours, and filtering off the sodium chloride precipitate from the resulting acyl nitrate solution.

Thermal Decomposition of Acyl Nitrates

Solutions of acyl nitrates were heated to boil under reflux in a stream of nitrogen; the released gases were washed with concentrated sulphuric acid and an aqueous solution of barium hydroxide. At an initial concentration of acyl nitrates 0·2 mol/l the decomposition reaction indicated by the formation of brown fumes of nitrogen oxides over the reaction mixture and of a precipitate of barium carbonate lasted some five to fourteen hours. After the decomposition was completed barium carbonate was filtered off, washed with water, and at 110°C dried to constant weight. Organic acids were extracted from the reaction mixture with 0·1м-NaOH, and their amount was determined gravimetrically; the acids were identified by their melting points or the "mixed" melting point, and by the results of elemental analysis. The greatest part of the solvent was removed by distillation from the reaction mixture freed from acids; the rest was filtered and analyzed on a chromatograph Chrom 3, manufactured by Laboratorní přístroje, Prague (column 1 200 mm, 10% Apiezon L on Chromosorb P, 180° and 150°C, 60 cm³ N₂/min). Peaks on the chromatograms were identified and calibrated with pure compounds. If no authentic compound was at disposal for a given peak, the corresponding product was isolated on a Perkin-Elmer F 90 gas chromatograph and identified by means of an A.E.I. MS-902 mass spectrograph. One part

of acid anhydride which crystallized from concentrated solutions after standing for some time in the refrigerator was determined gravimetrically; the rest of the anhydride in solution was determined by gel chromatography (column packing S-Gel-832 — Institute of Macromolelar Chemistry, Czechoslovak Academy of Sciences, Prague).

REFERENCES

1. Barlow L. R.: Tetrahedron *24*, 4913 (1968).
2. Gold V., Hughes E. D., Ingold C. K.: J. Chem. Soc. *1950*, 2467.
3. Gold V., Hughes E. D., Ingold C. K., Williams G. H.: J. Chem. Soc. *1950*, 2452.
4. Burton H., Praill P. F. G.: J. Chem. Soc. *1955*, 729.
5. Bamford C. H., White E. F. T.: J. Chem. Soc. London *1960*, 4490.
6. Bunce N. J., Tanner D. D.: J. Am. Chem. Soc. *91*, 6096 (1969).
7. Bunce N. J., Urban L. O.: Can. J. Chem. *49*, 821 (1971).
8. Clarke J. T., Howard R. O., Stockmayer W. H.: Makromol. Chem. *44—46*, 427 (1961).
9. Hrabák F., Vacek M.: This Journal *30*, 573 (1965).
10. Francis F. E.: J. Chem. Soc. *89*, 1 (1906); Ber. *39*, 3798 (1906).

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