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Intermediates in Reactions of Diacyl Peroxides with Tertiary Aliphatic Amines

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Abstract—*N*-Acyloxyammonium salts were isolated in reactions of diacyl peroxides with trialkylamines in the presence of sodium tetraphenylborate at low temperature. These salts are intermediates in reactions of organic peroxides with trialkylamines, which follow the nucleophilic substitution pattern.

Decomposition of organic peroxides by the action of tertiary amines follows single-electron transfer (SET) or nucleophilic substitution mechanism (S_N2). These mechanisms could not be distinguished by studying the reaction kinetics, effect of nucleophile nature, structure–reactivity relations, and effect of solvent polarity, as well as by detection of radical species [1, 2]. Experimental difficulties in distinguishing the above mechanisms are illustrated by Scheme 1 which shows different paths of product formation in the reaction of benzoyl peroxide with tertiary amines.

Because of fast establishment of equilibrium (1), analysis of the products gives no unambiguous information on the reaction mechanism, for effective recombination of radical pairs can conceal the SET-induced reaction; on the other hand, homolytic dissociation of the N−O bond in the intermediate formed by the S_N2 mechanism leads to appearance of radicals in the system.

In some cases, the mechanism of peroxide decomposition promoted by electron-donor compounds can be determined on the basis of the product structure, but unambiguous answer can be obtained in rare cases. In particular, the formation of pyridine *N*-oxide and benzoic anhydride in the reaction of pyridine with benzoyl peroxide indicates S_N2 mechanism of the process [2]. The formation of *N*-acyloxyammonium salts as intermediates in reactions of organic peroxides with amines is an important experimental proof for the nucleophilic substitution mechanism.

The formation of radicals in reactions of peroxides with tertiary amines was interpreted in [3, 4] in favor of the SET mechanism. *N*-Acyloxyammonium salts initiate radical polymerization of vinyl monomers, though the initiation efficiency is low [5]. The presence of radicals was also confirmed by the CIDNP method [3]. However, these data do not contradict the nucleophilic substitution mechanism. It is known that the yield of radical species in the system dimethyl-aniline–benzoyl peroxide is about 20%, and many authors believe that the reaction follows nucleophilic substitution mechanism [1, 6]. Moreover, the yield of the salt is too large to be explained in terms of the SET mechanism, followed by recombination of benzoyloxy radical and amine radical cation, as shown in Scheme 1. Initiation of radical polymerization is
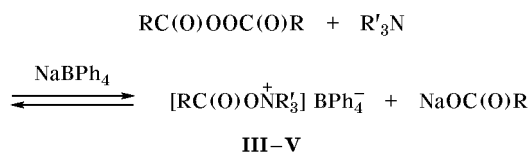
Scheme 1.
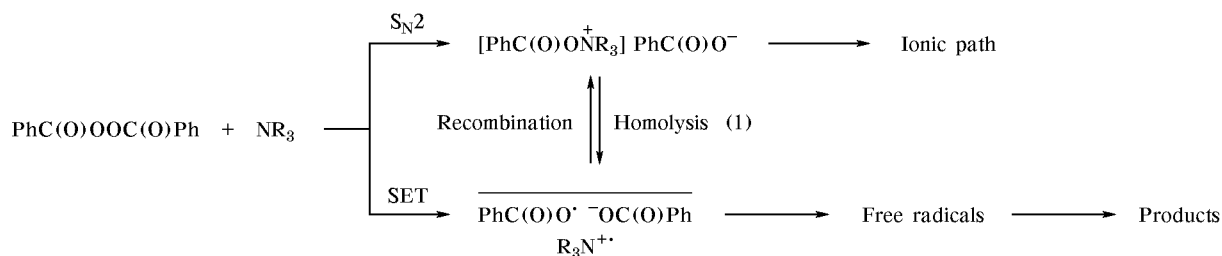
explained by homolytic dissociation of the cation at the N−O bond.

The goal of the present work was to study the mechanism of reaction of organic peroxides with tertiary amines and elucidate factors affecting this process. For this purpose, we examined reactions of benzoyl peroxide (**I**) and lauroyl peroxide (**II**) with triethylamine, tributylamine, and 2-dimethylamino-ethanol and tried to isolate intermediate products.

Acyloxyammonium salts are usually obtained by reactions of amine *N*-oxides with strong acylating agents, e.g., anhydrides [5, 7, 8]. However, such salts are difficult to isolate, for they undergo Polonovski reaction [8]. The yield of these salts can be improved by carrying out the reaction in the presence of sodium tetraphenylborate. For example, *N*-benzoyloxytriethyl-ammonium tetraphenylborate was isolated in the reaction of benzoyl peroxide with triethylamine in the presence of sodium tetraphenylborate [5]. *N*-Acetoxy-trimethylammonium bromide was obtained by reaction of acetyl peroxide with trimethylamine [9]. We succeeded in isolating and identifying intermediate *N*-acyloxyammonium salts stabilized by tetraphenyl-borate anion in reactions of diacyl peroxides with tertiary aliphatic amines (Scheme 2).

Scheme 2.

$$RC(O)OOC(O)R \ + \ R'_3N$$

$$\xrightleftharpoons{\text{NaBPh}_4} \ [RC(O)O\overset{+}{N}R'_3] \ BPh_4^- \ + \ NaOC(O)R$$

$$\textbf{III–V}$$

We isolated *N*-benzoyloxytriethylammonium tetra-phenylborate (**III**), *N*-benzoyloxytributylammonium tetraphenylborate (**IV**), and *N*-benzoyloxydimethyl-(2-hydroxyethyl)ammonium tetraphenylborate (**V**) in reactions of benzoyl peroxide with triethylamine, tributylamine, and 2-dimethylaminoethanol, respectively. Also, *N*-lauroyloxytriethylammonium tetra-phenylborate (**VI**) was obtained by reaction of lauroyl peroxide with triethylamine in the presence of sodium tetraphenylborate (Table 1).

The purity of the isolated salts was proved by the data of elemental analysis and IR spectroscopy. Their IR spectra showed no splitting of bands corresponding to stretching vibrations of the carbonyl group (1760 and 1775 cm^{-1} for benzoyl peroxide in acetonitrile and 1785 and 1800 cm^{-1} for lauroyl paroxide in dimethyl sulfoxide): only a single carbonyl band was present. The formation of salt in the reaction of ben-zoyl peroxide with triethylamine was also confirmed by sharp increase in the electric conductivity on mixing the reactants. An electrolytic cell was charged with 4.5 ml of a 0.1 M solution of benzoyl peroxide in acetonitrile. The resistance of the solution was 57 kΩ. After addition of 0.2 ml of triethylamine, the resistance of the resulting solution decreased by a factor of 150 and attained a value of 0.38 kΩ within a few seconds.

We failed to isolate intermediate *N*-acyloxyammo-nium salts in reactions of α,α-dimethylbenzyl per-oxide and *tert*-butyl peroxybenzoate with tertiary amines.

One of the ways of distinguishing SET and S_N2 mechanisms is based on analysis on the relation be-tween donor and acceptor properties of the reactants. Our results and published data indicate that the rate of the reaction of organic peroxides with amines and the product structure are related to ionization poten-tials of the amines and electron affinities of the peroxides [2, 6, 10], i.e., to electron-donor properties of the former and electron-acceptor properties of the latter. Srinivas and Taylor [6] presumed that the quantity Δ*G*, which is calculated as the difference between the oxidative potential of donor and reductive potential of acceptor, is the main factor determining the relative contributions of the S_N2 and SET paths.

Table 2 contains published data and our present results concerning the mechanism of reactions of

Table 1. Melting points, elemental analyses, and carbonyl stretching vibration frequencies of *N*-acyloxytrialkylammo-nium tetraphenylborates **III–VI**

Comp. no.	mp, °C	Found, %			Formula	Calculated, %			$\nu_{C=O}$, cm^{-1}
		N	C	H		N	C	H	
III	128	2.85	82.02	8.08	$C_{37}H_{40}BNO_2$	2.59	82.07	7.44	1765
IV	111	2.74	83.11	8.01	$C_{43}H_{52}BNO_2$	2.24	82.54	7.37	1775
V	182–184	2.86	79.62	7.01	$C_{35}H_{36}BNO_3$	2.65	79.39	6.87	1720
VI	178–180	2.26	81.29	9.18	$C_{42}H_{58}BNO_2$	2.26	81.40	9.43	1710

Table 2. Energies of frontier molecular orbitals of nucleophiles (HOMO) and peroxides (LUMO) and mechanisms of their reactions

Peroxide no.[a]	E_{LUMO}, eV	Nucleophile	E_{HOMO}, eV	ΔE, eV	Mechanism
I	–0.53	4-Cyanopyridine	–10.43	9.90	No reaction [2]
II	0.82	Triethylamine	–8.80	9.62	S_N2 [this work]
I	–0.53	Pyridine	–9.93	9.40	S_N2 [2]
I	–0.53	4-Methylpyridine	–9.89	9.36	S_N2 [2]
II	0.82	*N,N*-Dimethylaniline	–8.28	9.09	S_N2 [13]
I	–0.53	2-Dimethylaminoethanol	–9.19	8.66	S_N2 [this work]
VIII	–0.83	1-Azabicyclo[2.2.2]octane	–9.41	8.58	S_N2 [6]
I	–0.53	Triethylamine	–8.80	8.27	S_N2 [this work]
VIII	–0.83	1,4-Diazabicyclo[2.2.2]octane	–9.00	8.18	S_N2 [6]
I	–0.53	Tributylamine	–8.70	8.17	S_N2 [this work]
VII	–0.48	Dimethyl sulfide	–8.48	8.00	SET [1]
I	–0.53	Dimethyl sulfide	–8.48	7.95	S_N2 [1]
I	–0.53	*N,N*-Dimethylaniline	–8.28	7.74	S_N2 [1, 6] SET [4, 14]
VIII	–0.83	*N,N*-Dimethylaniline	–8.28	7.45	S_N2 [6]
VIII	–0.83	*N,N,N',N'*-Tetramethyl-1,4-phenylenediamine	–7.67	6.84	SET [6]
IX	–2.14	Dimethyl sulfide	–8.48	6.34	SET [1]

[a] *tert*-Butyl peroxybenzoate (**VII**), cyclobutanecarbonyl *m*-chloroperoxybenzoate (**VIII**), *tert*-butyl 3,5-dinitroperoxybenzoate (**IX**).

peroxides with various nucleophiles. Electron-donor properties of amines can be related to the energies of their highest occupied molecular orbitals (HOMO), while electron-acceptor properties of peroxides can be related to the energies of their lowest unoccupied molecular orbitals (LUMO). Therefore, we tried to correlate the reaction mechanism with the difference ΔE between the HOMO energy (E_{HOMO}) of the nucleophile and LUMO energy (E_{LUMO}) of the peroxide. The electronic parameters were calculated by the AM1 method [11] with full geometry optimization. Table 2 contains the calculated HOMO and LUMO energies and the corresponding differences for the compounds studied in the present work; for comparison, published data are given for reactions whose mechanism is known [1, 2, 6, 12–14].

As follows from Table 2, S_N2 mechanism is operative when $\Delta E > 8$ eV; two mechanisms are possible when 8 eV $> \Delta E > 6.84$ eV; and the reaction takes the SET path when $\Delta E < 6.84$ eV. The ΔE values for the reactions of benzoyl peroxide and lauroyl peroxide with triethylamine, tributylamine, and 2-dimethyl-aminoethanol are 8.17 eV and higher, i.e., they fall into the range corresponding to the S_N2 mechanism.

Thus, the isolation of acyloxyammonium salts in reactions of diacyl peroxides with amines and the results of theoretical analysis of the MO energies can be regarded as reliable proofs for nucleophilic substitution mechanism of these reactions.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-71 spectrometer from solutions in acetonitrile and dimethyl sulfoxide using CaF_2 cells (layer thickness 0.51 cm). The melting points were determined with the aid of a Boetius heating device coupled with an RNMK 05 microscope. Toluene and ethanol were dehydrated and purified by standard procedures [15]. Benzoyl and lauroyl peroxides were recrystallized twice from ethanol. Their purity was checked by iodometry. Trialkylamines were purified by the procedures recommended in [16].

Reaction of diacyl peroxides with tertiary amines. The reactions were carried out in ethanol–toluene (1:1) at –5°C. A mixture of 3 mmol of appropriate peroxide in 15 ml of toluene and 3 mmol of sodium tetraphenylborate in 5 ml of ethanol was cooled to –5°C. A solution of 3 mmol of trialkylamine in 10 ml of ethanol was added dropwise over a period of 3 h, maintaining the temperature at –5°C. After 30 h, the precipitate was filtered off and washed with water to remove sodium benzoate and then with cold methanol. Yield 26–30%.

REFERENCES

1. Pryor, W.A. and Hendrickson, W.H., *J. Am. Chem. Soc.,* 1983, vol. 105, p. 7114.

2. Vidal, S., Court, J., and Bonnier, J.M., *Tetrahedron,* 1984, vol. 40, p. 4911.

3. Markaryan, Sh.A., *Zh. Org. Khim.,* 1982, vol. 18, p. 252.

4. Horner, L.J., *J. Polym. Sci.,* 1955, vol. 18, p. 438.

5. Sato, T. and Otsu, T., *Macromol. Chem.,* 1970, vol. 137, p. 43.

6. Srinivas, S. and Taylor, G.K., *J. Org. Chem.,* 1990, vol. 55, p. 1779.

7. Oae, S., Asai, N., and Fujimori, K., *Bull. Chem. Soc. Jpn.,* 1979, vol. 52, p. 2409.

8. Huisgen, R. and Kolveck, W., *Tetrahedron Lett.,* 1965, p. 783.

9. Walton, B. and Geiger, *J. Org. Chem.,* 1958, vol. 23, p. 299.

10. Beileryan, N.M., *Kinet. Katal.,* 1997, vol. 38, p. 32.

11. Stewart, J.J.P., *MOPAC 93 Manual,* 1993.

12. Aleksandrov, Yu.A., Gorbatov, V.V., and Yablokova, N.V., *Dokl. Akad. Nauk SSSR,* 1980, vol. 250, p. 6236.

13. Sato, T., Kita, S., and Otsu, T., *Macromol. Chem.,* 1975, vol. 176, p. 561.

14. Graham, D.M. and Mesrobian, R.B., *Can. J. Chem.,* 1963, vol. 41, p. 2938.

15. Gordon, A.J. and Ford, R.A., *The Chemist's Companion,* New York: Wiley, 1972.

16. Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., Jr., *Organic Solvents: Physical Properties and Methods of Purification,* New York: Intersci., 1955, 2nd ed.