Preparation and Properties of Acyl Carbamoyl Peroxides: a Novel Type of Peroxide

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Summary Acyl carbamoyl peroxides are formed by addition of peroxy-acids to isocyanates, and benzoyl *N*-(*p*-nitrophenyl)carbamoyl peroxide shows a decomposition pattern indicating the intermediacy of an amino-radical, a nitrene, and a protonated nitrene.

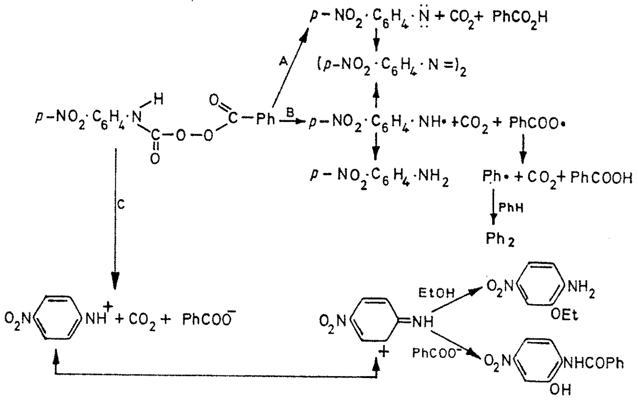
PEROXY-ACIDS have been found to react with isocyanates in ether at −15° with a trace of pyridine as catalyst to give acyl carbamoyl peroxides, a new type of peroxide.

$$R^1NCO + R^2CO_3H \longrightarrow R^1NH{\cdot}C(:O)OOC(:O){\cdot}R^2$$

A typical procedure is as follows: a solution of peroxybenzoic acid in ether (8·0 g. in 50 ml.) was added to a stirred solution of *p*-nitrophenyl isocyanate in ether (8·9 g. in 150 ml.) containing two drops of pyridine, and the precipitated benzoyl *N*-(*p*-nitrophenyl)carbamoyl peroxide (I) (9·1 g., 55%) was collected and recrystallized from dichloromethane between 0° and −78°.

Peroxides similarly prepared, together with relevant data, are listed in the Table. All of them decompose rapidly at room temperature evolving carbon dioxide and turning brown. At the temperature of solid carbon dioxide, however, they are quite stable over a long period of time. The half-life of peroxide (I) at room temperature is about 40 hr., indicating that peroxide (I) is much less stable than t-butyl *N*-(*p*-nitrophenyl)peroxycarbamate (half-life about 600 days at room temperature).[1,2]

All the peroxides prepared are relatively stable in such solvents as benzene, chloroform, carbon tetrachloride, ether, and acetic acid, whereas they decompose very rapidly in strongly polar solvents, such as ethanol, acetone, and acetonitrile, and explosively in dimethylaniline.



Products from thermal decomposition of (I) in crystalline state and in solution were: in crystalline state at room temperature, carbon dioxide (II, 98%), benzoic acid (III, 80%), *pp*′-dinitroazobenzene (IV, 30%), and a trace of *p*-nitroaniline (V); in benzene at 80°, (II; 117%), (III; 48%), biphenyl (20%), (IV; 24%), and (V; 15%); in ethanol at 78°, (II; 96%), (III; 68%), 5-nitro-2-benzamidophenol

Preparation and properties of acyl carbamoyl peroxides $R^1NHC(:O)OOC(:O)\cdot R^2$

R^1	R^2	Yield (%)	Solvent[a]	d.p. (°c)[b]	Purity[c]
p-$NO_2\cdot C_6H_4$	Ph	55	A	63	98%
p-$CN\cdot C_6H_4$	,,	57	A	51	93
p-$CO_2Et\cdot C_6H_4$	,,	56	A	55	96
m-$Cl\cdot C_6H_4$	,,	55	B		[d]
o-$NO_2\cdot C_6H_4$	,,	69	A	64	94
p-$NO_2\cdot C_6H_4$	p-$MeO\cdot C_6H_4$	68	A	68	100
,,	p-MeC_6H_4	86	A	64	94
,,	m-$Cl\cdot C_6H_4$	40	C	60	97
,,	p-$NO_2\cdot C_6H_4$	19	D	55	84
,,	n-$C_{11}H_{23}$	47	D	49	95
PhCO	Ph	75	D	60	97
$PhSO_2$	,,	74	D	80	82

[a] Solvent for recrystallization: A, dichloromethane; B, ether and light petroleum; C, dichloromethane and light petroleum; D, ether. [b] Decomposition point: all peroxides decompose explosively at these temperatures except for $R^1 = PhSO_2$, $R^2 = Ph$. [c] Active oxygen estimated by iodometry in acetic acid.[3] Satisfactory elemental analyses were obtained. [d] Too unstable to be submitted to analysis.

(10%), and 5-nitro-2-aminophenethole (63%). These results seem to suggest that (I) decomposes *via* three different mechanisms A, B, and C depending on the reaction conditions.

In all probability, the decomposition proceeds *via* path A in crystalline state, *via* paths A and B in benzene, and *via* path C in ethanol. Path A is a new mode for generation of a nitrene intermediate.

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[3] A. T. Blomquist and A. F. Ferris, *J. Amer. Chem. Soc.*, 1951, **73**, 3408.