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Generation of Peroxy Radicals from Peroxynitrates ($ROONO_2$). Decomposition of Peroxybenzoyl Nitrate (PBzN)

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Abstract: At ambient temperatures peroxybenzoyl nitrate (PBzN) is in equilibrium with benzoylperoxy radicals and NO_2. In the presence of radical scavengers such as NO or $^{15}NO_2$, the equilibrium is perturbed and the disappearance of PBzN is determined by the O–NO_2 homolysis rate constant (k_1). In this manner the rate constant has been evaluated from 291 to 314 K and found to be $k_1/s^{-1} = 10^{(15.2\pm0.60)}e^{(-25900\pm910/RT)}$. The rate constant for reaction of NO with benzoylperoxy radical (k_2) has been measured relative to the rate constant for reaction of NO_2 (k_{-1}) and found to be 1.52 ± 0.12 at 250 K. From these data and estimates of ΔS_1, k_{-1} and k_2 have been calculated to be $\sim 1 \times 10^9$ M^{-1} s^{-1} and $\sim 1.5 \times 10^9$ M^{-1} s^{-1}, respectively. In the presence of NO_2, the loss of PBzN by reaction 1 is retarded and the decomposition rate parameters observed are more typical for a wall-catalyzed reaction than a homolytic process. From these experiments it is clear that O–ONO_2 cleavage is extremely slow; the limit for O–NO_2 cleavage relative to O–ONO_2 cleavage is >27 at 303 K.

Interest in the chemistry of peroxynitrates, $ROONO_2$, dates to 1955[1,2] when Stephens and co-workers discovered the so-called "compound X", which was later[3,4] identified as peroxyacetyl nitrate [PAN; R = $CH_3C(O)$], a product derived from irradiation of hydrocarbon–NO_2–air mixtures. The observation that PAN was a constituent of photochemical smog[5] spurred investigation of PAN and its various homologues (e.g., peroxypropionyl and peroxybutyryl nitrate).[6] For the most part, these studies focused on PAN as a *product* of photochemical smog and were confined to methods for preparation[4,7-10] and analysis[11-18] of PAN, its biological activity,[19-23] and various solution-phase reactions of PAN.[21,24-28] Only recently has attention focused on the gas-phase free-radical chemistry of PAN and on the role played by PAN in the *formation* of photochemical smog. Based on work performed by three different groups,[29-31] it is now clear that PAN exists in dynamic equilibrium with acetylperoxy radicals (ROO·) and NO_2, reaction 1,–1. Moreover, the fate of PAN in the

$$ROONO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ROO\cdot + NO_2 \qquad (1,-1)$$

troposphere is determined by partitioning of acetylperoxy radicals between reaction –1 with NO_2 to form PAN and reaction 2 with NO to form NO_2, and acetoxy radicals (RO·). These conclusions were based on the observation that radical scavengers such as NO and $^{15}NO_2$ enhance the rate of disappearance of PAN.

$$ROO\cdot + NO \rightarrow RO\cdot + NO_2 \qquad (2)$$

The revelations regarding the gas-phase chemistry of PAN were followed by similar research on related peroxynitrates, including peroxynitric acid (R = H),[32-35] peroxychloroformyl nitrate [R = ClC(O)–],[36] and peroxy-*tert*-butyl nitrate.[37] These peroxynitrates were also shown to be in equilibrium with NO_2 and the respective peroxy radicals, indicating that O–N bond homolysis is a general phenomenon for this class of compounds.

Peroxybenzoyl nitrate [PBzN; R = $C_6H_5C(O)$–] is an important peroxynitrate and an excellent model for aromatic peroxynitrates that have not been investigated. PBzN and other peroxyaroyl nitrates are potent lachrymators,[38,39] and they been implicated in the enhanced level of eye irritation associated with photochemical reactions of gaseous aromatic hydrocarbons. With the increased use of aromatic hydrocarbons in automotive fuels, the formation of PBzN and related compounds in polluted urban atmospheres becomes an important consideration. Accordingly, we felt it important to investigate the gas-phase free-radical chemistry of PBzN. Our goals were to (1) evaluate the mechanism and kinetics of the decomposition and formation of PBzN, (2) determine the extent to which reaction 1,–1 predominates over other possible homolytic reactions such as O–O cleavage, reaction

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† Deceased.

(1) E. R. Stephens, P. L. Hanst, R. C. Doerr, and W. E. Scott, *Ind. Eng. Chem.* **48**, 1498 (1956).

(2) E. R. Stephens, W. E. Scott, P. L. Hanst, and R. C. Doerr, *J. Air Pollut. Control Assoc.*, **6**, 159 (1956).

(3) E. R. Stephens, E. F. Darley, O. C. Taylor, and W. E. Scott, *Proc. Am. Pet. Inst.*, **4**, 325 (1960).

(4) E. R. Stephens, E. F. Darley, O. C. Taylor, and W. E. Scott, *Int. J. Air Water Pollut.* **4**, 79 (1961).

(5) W. E. Scott, E. R. Stephens, P. L. Hanst, and R. C. Doerr, *Proc. Am. Petrol. Inst., Sect.* III, **37**, 171 (1953).

(6) E. R. Stephens, *Adv. Environ. Soc. Technol.*, **1**, 119 (1969).

(7) E. R. Stephens, F. R. Burleson, and E. A. Cardiff, *J. Air Pollut. Control Assoc.*, **15**, 87 (1965).

(8) C. A. Tuesday, "Chemical Reactions in the Lower and Upper Atmosphere", Interscience, N.Y., 1961, p 15.

(9) B. W. Gay, R. C. Noonan, J. J. Bufalini, and P. L. Hanst. *Environ. Sci. Technol.*, **10**, 82 (1976).

(10) R. Louw, G. J. Sluis, and H. P. W. Vermeeren, *J. Am. Chem. Soc.*, 97, 4396 (1975).

(11) E. R. Stephens and M. A. Price, *J. Chem. Educ.*, **50**, 351 (1973).

(12) E. F. Darley, K. A. Ketner, and E. R. Stephens, *Anal. Chem.*, **35**, 589 (1963).

(13) J. N. Pitts, H. Fuhr, J. S. Gafney, and J. W. Peters, *Environ. Sci. Technol.*, **7**, 550 (1973).

(14) S. A. Penkett, F. J. Sandalls, and J. E. Lovelock, *Atmos. Environ.*, **9**, 139 (1975).

(15) O. C. Taylor, *J. Air Pollut. Control Assoc.*, **19**, 347 (1969).

(16) D. T. Tingey and A. C. Hill, *Proc. Utah Acad. Sci., Arts, Lett., V*, **44**, Part 1, 387 (1967).

(17) W. A. Lonneman, J. J. Bufalini, and R. L. Seila, *Environ. Sci. Technol.*, **10**, 374 (1976).

(18) H. Nieboer and J. van Ham, *Atmos. Environ.*, **10**, 115 (1976).

(19) K. I. Campbell, G. L. Clarke, L. O. Emik, and R. L. Plata, *Arch. Environ.* Health, **15**, 739 (1967).

(20) A. Kruysse, V. J. Ferron, H. R. Immel, B. J. Spit, and G. J. Van Esch, *Toxicology*, **8**, 231 (1977).

(21) J. B. Mudd in "*Free Radical Biology*", Vol. II, W. A. Pryor, Ed., Academic Press, N.Y., 1976, p 203.

(22) E. F. Darley, W. M. Dugger, J. B. Mudd, L. Ordin, O. C. Taylor, and E. R. Stephens, *Arch. Environ. Health*, **6**, 761 (1963).

(23) E. A. Schuck, E. R. Stephens, and J. T. Middleton, *Arch. Environ. Health*, **13**, 570 (1966).

(24) S. W. Nicksic, J. Harkins, and P. K. Mueller, *Atmos. Environ.*, **1**, 11 (1967).

(25) E. R. Stephens, *Atmos. Environ*, **1**, 19 (1967).

(26) R. P. Steer, K. R. Darnall, and J. N. Pitts, *Tetrahedron Lett.*, 3765 (1969).

(27) P. H. Wendschuh, C. T. Pate, and J. N. Pitts, *Tetrahedron Lett.*, 2931 (1973).

(28) K. R. Darnall and J. N. Ptts, *Chem. Commn.*, 1305 (1970).

(29) R. A. Kenley and D. G Hendry, *J. Am.* Chem. *Soc.*, **99**, 3198 (1977).

0002-7863/82/1504-0220$01.25/0

Table I. Observed Rate Constants (k_{obsd}) for Decomposition of PBzN at Various Temperatures in the Absence of Added Reactants[b]

run no.	temp, K	10^7-[PBzN], M	10^5-k_{obsd}, s^{-1}
1	280.8	2.69	0.279
2	293.1	5.30	1.05
3	303.6	9.24	2.02
4	303.6	11.4	1.63
5	313.8	8.76	3.64
6	323.4	5.78	10.3
7	323.4	3.88	12.1
8	333.7	5.08	31.6
9	333.7	4.67	27.4

[a] k_{obsd} calculated from eq 10, see text. [b] Argon added as diluent gas to total pressure of 800 torr.

Table II. Observed Rate Constants (k_{obsd})[a] for Decomposition of PBzN at Various Temperatures in the Presence of NO[b]

run no.	temp, K	10^7-[PBzN], M	10^5-[NO], M		$10^5 k_{\mathrm{obsd}}$, s^{-1}
1	291.3	4.97	65.2		6.33
2	291.3	5.28	26.3		8.18
3	291.3	4.37	19.6		7.76
4	291.3	5.20	8.83		8.53
5	291.3	3.06	8.83		8.04
6	291.3	3.56	8.83		10.2
				av	8.18 ± 1.2
7	298.8	3.02	24.3		16.4
8	298.8	5.94	15.2		15.2
9	298.8	3.79	11.6		14.7
10	298.8	4.15	20.7		17.4
				av	15.9 ± 1.2
11	303.6	3.30	12.7		46.8
12	303.6	3.33	24.3		34.6
13	303.6	5.28	20.2		31.8
14	303.6	4.26	15.2		38.5
15	303.6	3.68	17.2		40.4
				av	36.2 ± 3.3
16	308.6	3.77	15.2		77.5
17	308.6	3.78	11.6		79.0
18	308.6	3.61	24.3		71.9
19	308.6	4.39	19.7		72.5
				av	75.2 ± 3.6
20	313.8	2.17	15.2		125
21	313.8	3.24	11.6		139
22	313.8	4.15	17.2		154
23	313.8	3.28	19.7		181
24	313.8	4.26	20.7		148
				av	142 ± 13

[a] Calculated from eq 10. [b] Argon added as dilutent to a total pressure of 800 torr.

3, and (3) estimate the significance of these homolyses with respect to the fate and reactivity of PBzN in the troposphere.

$$\mathrm{ROONO_2} \rightarrow \mathrm{RO\cdot} + \mathrm{NO_3} \tag{3}$$

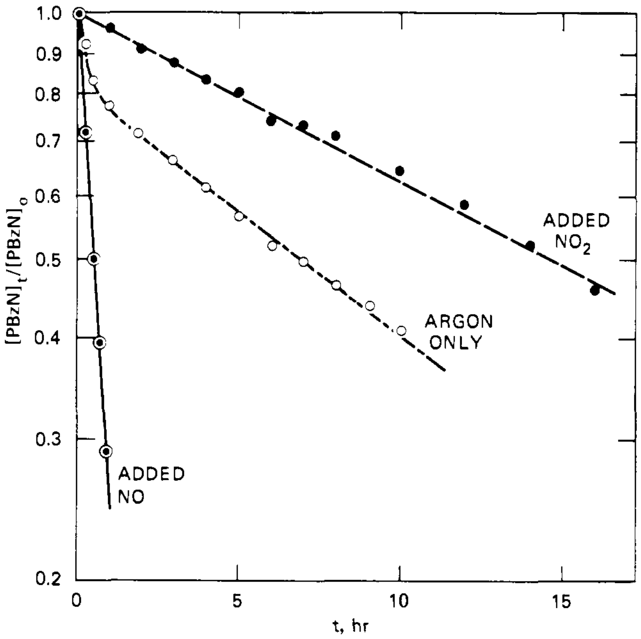

Figure 1. Semilogarithmic plot of fraction of PBzN remaining ($[PBzN]_t/[PBzN]_0$) for decomposition of PBzN at 303.6 K in the presence of: argon only (○- - -○), data of Table I run 3; added NO (⊙—⊙), data of Table II run 11; and added NO_2 (●- -●), data of Table III run 2.

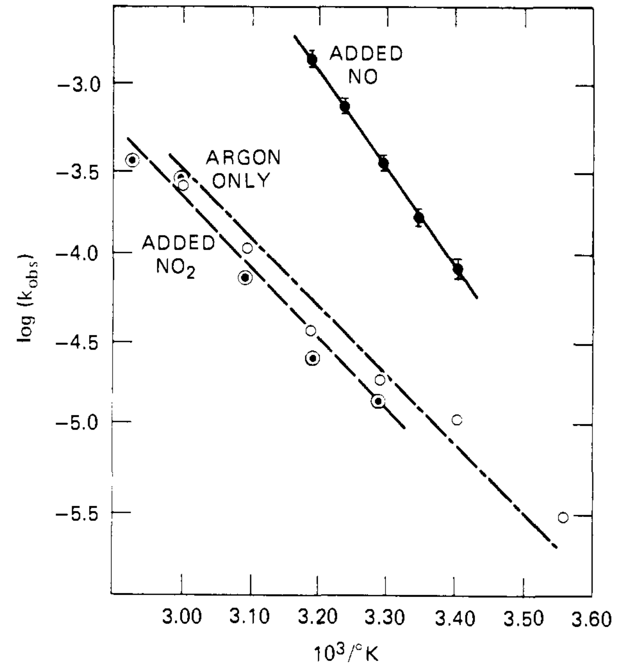

Figure 2. Log (k_{obsd}), s^{-1}, vs. $1/T(K^{-1})$ for decomposition of PBzN: with added NO (●—●); with added NO_2 (⊙- -⊙); with argon only (○- - -○).

Results and Discussion

General Approach. Possible loss mechanisms for PBzN in the absence and presence of NO as a radical scavenger are represented by reactions 1,–1 to 6.

$$\mathrm{C_6H_5C(O)OONO_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C_6H_5C(O)OO\cdot} + \mathrm{NO_2} \tag{1,–1}$$

$$\mathrm{C_6H_5C(O)OO\cdot} + \mathrm{NO} \xrightarrow{k_2} \mathrm{C_6H_5C(O)O\cdot} + \mathrm{NO_2} \tag{2}$$

$$\mathrm{C_6H_5C(O)OONO_2} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{C_6H_5C(O)O\cdot} + \mathrm{NO_3} \tag{3,–3}$$

$$\mathrm{C_6H_6C(O)O\cdot} + \mathrm{NO} \xrightarrow{k_4} \mathrm{C_6H_5C(O)ONO} \tag{4}$$

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(30) R. A. Cox and M. J. Roffey, *Environ. Sci. Technol.*, **11**, 901 (1977).

(31) C. T. Pate, R. Atkinson, and J. N. Pitts, *J. Environ. Health Sci., Environ. Sci. Eng. R.*, **A 11** (1), 19 (1976).

(32) H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenback, *Chem. Phys.* Lett., **45**, 546 (1977).

(33) P. L. Hanst and B. W. Gay, *Environ. Sci. Technol.*, **11**, 1105 (1977).

(34) R. A. Graham, A. M. Winer, and J. N. Pitts, *Chem. Phys. Lett.*, **51**, 215 (1977).

(35) R. A. Graham, A. M. Winer, and J. N. Pitts, *J. Chem. Soc.*, **68**, 4505 (1978).

(36) J. W. Spence, E. O. Edney, and P. L. Hanst, *Chem. Phys. Lett.*, **56**, 478 (1978).

(37) R. A. Kenley and D. G. Hendry, unpublished observations.

(38) J. M. Heuss and W. A. Glasson, *Environ. Sci. Technol.*, **2**, 1109 (1968).

(39) W. A. Glasson and J. M. Heuss, *Environment Sci. Technol.*, **11**, 395 (1977).

$$C_6H_5C(O)O\cdot \xrightarrow{k_5} C_6H_5\cdot + CO_2 \tag{5}$$

$$2C_6H_5C(O)OO\cdot \xrightarrow{k_6} 2C_6H_5C(O)O\cdot + O_2 \tag{6}$$

The reverse of reaction 3 must compete with the unimolecular decarboxylation of $C_6H_5C(O)O\cdot$ ($k_5 = 1 \times 10^7$ s^{-1} at 300 K)[40,41] and the reaction of NO_3 with NO and NO_2. Under all conditions these reactions will dominate reaction −3. Benzoylperoxy radicals, however, are not prone to unimolecular decomposition, and recombination with NO_2 to reform PBzN by reaction 1,−1 involves an equilibrium that can be perturbed by scavenging $C_6H_5C(O)OO\cdot$, e.g., by reaction 2. However, if decomposition occurs via reaction 3,−3, the rate of disappearance of PBzN will follow strictly first-order kinetics and the rate will be unaffected by radical scavengers; that is, the rate will be as described in eq 7. If reaction

$$-d[\mathrm{PBzN}]/dt = k_3[\mathrm{PBzN}] \tag{7}$$

1,-1 is operative, however, loss of PBzN in the absence of scavengers will ultimately be via reaction 6. In this case, quadratic terms appear in the kinetic expression and first-order decay need not be observed. In the presence of a scavenger such as NO, where $k_2[NO][C_6H_5C(O)OO\cdot] \gg k_6[C_6H_5C(O)OO\cdot]^2$, the rate of disappearance of PBzN will be governed by eq 8. When [NO]

$$-d[\mathrm{PBzN}]/dt = k_1[\mathrm{PBzN}]\{k_2[\mathrm{NO}]/(k_2[\mathrm{NO}] + k_{-1}[\mathrm{NO_2}])\} \tag{8}$$

is sufficiently high that $k_2[NO] \gg k_{-1}[NO_2]$, eq 8 reduces to eq 9. Here, the rate of PBzN decomposition is zero order in [NO]

$$-d[\mathrm{PBzN}]/dt = k_1[\mathrm{PBzN}] \tag{9}$$

and first order in [PBzN], and the disappearance of PBzN is controlled by k_1, the rate constant for O–N cleavage. However, when $k_2[NO]$ does not greatly exceed $k_{-1}[NO_2]$, the rate of PBzN disappearance is no longer zero order in [NO], and the observed rate constant for PBzN decomposition is less than k_1 by the factor $k_2[NO]/(k_{-1}[NO_2] + k_2[NO])$ as seen in eq 8.

Effect of NO and NO_2 on Homolysis. In probing the effect of NO and NO_2 on homolysis, we first studied the temperature dependence of the kinetics of PBzN disappearance in the presence of argon as diluent gas but in the absence of added reactants. As described in the experimental section, we followed PBzN decay by IR, monitoring the 990-cm^{-1} band as a function of time. The decomposition was also followed at different temperatures with NO added as a peroxy radical scavenger, and with NO_2 added to suppress any contributions to the rate of decomposition via reactions 1,−1 and 6. In all cases, the rates of disappearance of PBzN were expressed in terms of an observed first-order rate constant, k_{obsd}, where k_{obsd} was determined from the slope of a semilog plot of the fraction of PBzN remaining vs. time [eq 10].

$$\ln([\mathrm{PBzN}]_t/[\mathrm{PBzN}]_0) = k_{obsd}t \tag{10}$$

Values of k_{obsd} so obtained are summarized in Tables I–III along with the various reaction conditions used. The semilog plots were linear to at least 2 half-lives of the PBzN for the reactions where NO and NO_2 were added. For PBzN decompositions in the absence of added reactants, however, the plots showed a linear decay only after an initial rapid decrease in [PBzN]. Examples of the decomposition of PBzN under the various conditions are shown in Figure 1. The temperature dependence of k_{obsd} for all these sets of reactions conditions is depicted in the Arrhenius plot in Figure 2. From the figure it is possible to calculate apparent activation parameters for the rate constants in question, and these are summarized in Table IV.

Table III. Observed Rate Constants (k_{obsd})^a for Decomposition of PBzN at Various Temperatures in the Presence of NO_2^{b}

run no.	temp, K	10^7-[PBzN], M	10^7-[NO_2], M	10^5-k_{obsd}, s^{-1}
1	303.6	5.65	8.52	1.34
2	303.6	3.81	15.8	1.35
3	313.8	7.22	11.2	2.42
4	323.4	7.17	6.62	7.22
5	332.7	7.34	17.5	29.6
6	341.7	6.29	3.85	34.1

^{a} k_{obsd} calculated from eq 10. ^{b} Argon added as diluent gas to a total pressure of 800 torr.

Table IV. Apparent Arrhenius Activation Energies (E_a) and Preexponential Factors (A) for Decomposition of PBzN in the Absence of Added Reactants and in the Presence of NO and NO_2^{a,b}

conditions	E_a, kcal/mol	log A, s^{-1}
argon only	16.2 ± 1.5	7.0 ± 0.6
added NO_2	18.9 ± 1.9	8.8 ± 1.3
added NO	25.9 ± 0.91	15.2 ± 0.60

^{a} Calculated from the expression $k_{obsd} = A \exp[-E_a/RT]$. ^{b} See Figure 2.

Several conclusions can be drawn from these data. First, it is evident that the decomposition of PBzN is greatly accelerated by addition of NO in excess of the initial [PBzN]. Furthermore, this decomposition is first-order in [PBzN] and zero order in [NO] over a very wide range of [NO]/[PBzN] ratios. As noted above, this behavior is consistent with PBzN homolysis involving O–N scission reaction 1,-1 and with the kinetic expressions given in eq 8 and 9. Entirely analogous situations were observed for decompositions of PAN,[29,30] pernitric acid,[35] and peroxycholoroformyl nitrate.[36] For PAN we observed that $k_1 = 10^{16.29}e^{-26910/RT}$. At 303.6 K, for PAN, $k_1 = 70.5 \times 10^{-5}$ s^{-1}, and from Table III for PBzN at the same temperature $k_1 = 36.2 \times 10^{-5}$ s^{-1}. Thus relative to PAN, PBzN is approximately two times more stable with respect to O–N homolysis. Referring to Table IV, we see that the relative stabilization of PBzN is attributed to a lower A factor (log A/s^{-1} = 15.2) since the activation energy for PBzN is E_a = 25.9 kcal/mol, a value somewhat lower than that for PAN. Also, in our earlier studies with PAN, we established the upper limit for k_3 (the rate constant for O–O homolysis) as being equal to the value of k_{obsd} obtained in the absence of added reactant. For PAN at 298 K, the ratio of rate constants is $k_1/k_3 \geq 250$. In the present example we set as an upper limit for k_3 the value of k_{obsd} obtained in the presence of added NO_2. The NO_2 should suppress any contributions of k_1 and k_6 to the overall rate of disappearance. Thus, for PBzN at 303.6 K, $k_1/k_3 \geq 27$. However, the apparent activation parameters for k_{obsd} for decomposition of PBzN in the presence of added NO_2 are E_a = 18.9 ± 1.9 kcal/mol and log A/s^{-1} = 8.8 ± 1.3. The A factor is impossibly low for a homolytic bond cleavage of the type required for reaction 3,[42] and this suggests that wall reactions must be responsible for destruction of PBzN under conditions where sufficient NO_2 is present to shift equilibrium 1,−1 to the left and thereby effectively prohibit decomposition by radical–radical reaction in the gas phase. Thus, the value of k_1/k_3 must be actually significantly higher than 27 in the gas phase and may be closer to the value of $k_1/k_3 \geq 250$ seen for PAN. The fact that the decomposition of PBzN in the absence of added reactants is not first order can be explained by losses via reaction 6 in the early stages of the reaction, with concomitant accumulation of NO_2. Once the concentration of accumulated NO_2 is sufficiently high, reaction −1 will predominate over reaction 6 and decomposition via wall reactions and/or reaction 3 will ensue.

Products of Decomposition. Formation of NO_2 (evidenced by its absorption at 1630 cm^{-1}) and CO_2 (2350 cm^{-1}) accompanied the decomposition of PBzN. The ratio of CO_2 formed to PBzN consumed was readily determined, as well as the rate of evolution of CO_2 for decompositions carried out at 303.6 K in the presence of excess NO. Values of k_{obsd} were obtained from the observed

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(40) C. F. Poranski, Jr., W. B. Moniz, and S. A. Sojka, *J. Am. Chem. Soc.*, **97**, 4275 (1975).

(41) R. E. Schwerzel, R. G. Lawler, and G. T. Evans, *Chem. Phys. Lett.*, **29**, 106 (1974); authors observed $k_5 \simeq 10^8$ s^{-1} at 403 K, and assuming an activation energy of 8.0 kcal/mol, one obtains log k_5 at 300 K.

(42) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley-Interscience, N.Y., 1976.

Table V. Observed Rate Constants (k_{obsd}) for Evolution of CO_2 from Decomposition of PBzN at 303.6 K and 800 torr Total Pressure in the Presence of Added NO

run no.	10^7-$[\mathrm{PBzN}]_0$, M	10^5-[NO], M	$\Delta CO_2/\Delta$PBzN	$10^4 k_{\mathrm{obsd}}$,[a] s^{-1}
1	6.29	25.8	0.673	3.49
2	6.80	540	0.639	3.29
3	6.96	2630	0.576	4.27
4	7.05	4220	0.622	4.17
		av	0.63 ± 0.04 av	3.79 ± 0.51

[a] Values of k_{obsd} obtained from semilog plots of $(A_t - A_0)/(A_\infty - A_0)$, where A is the absorbance at 2350 cm^{-1}.

absorbance at 2350 cm^{-1} using semilog plots of the fraction of total CO_2 evolved $(A_t - A_0)/(A_\infty - A_0)$ vs. time. Data for these experiments are summarized in Table V.

If benzoyloxy is a true intermediate formed in reaction 2, we would expect its reaction with NO (reaction 4) to be competitive with reaction 5. The ratio of rates of these two reactions should be

$$R_4/R_5 = k_4[\mathrm{NO}]/k_5 \tag{11}$$

The best estimate of k_4 is 5×10^9 M^{-1} s^{-1} based on data for simple alkoxy radicals.[43] the only estimates for k_5 are from liquid-phase experiments, where most recent data indicate a value of 1×10^7 s^{-1}.[40,41] Thus, over the NO concentration range reported in Table V, the k_4/k_5 ratio is expected to range from a low value of about 0.1 to a high value of 20. The ratios correspond to a CO_2 yield from 88% down to 1%, respectively.

From Table V it is clear that NO concentration has no effect on the CO_2 yield. The measured yield of CO_2 relative to the consumed PBzN equals 0.63 independent of the amount of NO. However, because of uncertainties in the extinction coefficients of CO_2 and PBzN, we cannot be certain that this value is significantly different from unity. In any event, one must conclude that if liquid-phase values of k_5 apply, thermalized benzoyloxy radicals are not likely intermediates in these reactions, and must be formed with sufficient energy to decompose before distributing their energy to the bath gas. Alternatively k_5 in the gas phase may be much faster than in the liquid phase.

$^{15}NO_2$-Exchange Reaction. As final proof in the importance of equilibrium 1,−1 in the reactions of PBzN, we have studied the exchange between PBzN and ^{15}N-Labeled NO_2. If $^{15}NO_2$ is added to PBzN in argon, incorporation of label into the PBzN with liberation of unlabeled NO_2 should occur as shown below.

$$C_6H_5C(O)OONO_2 \rightleftarrows C_6H_5C(O)OO\cdot + NO_2 \quad (1,-1)$$

$$C_6H_5C(O)OO^{15}NO_2 \rightleftarrows C_6H_5C(O)OO\cdot + {}^{15}NO_2 \quad (1,-1)^*$$

By applying the steady-state approximation to $C_6H_5C(O)OO\cdot$, we obtain the kinetics of the exchange reaction as shown in eq 12. When $^{15}NO_2$ is added in excess of PBzN, initially $[^{15}NO_2]$

$$d[\mathrm{PBzN}^*]/dt = -d[\mathrm{PBzN}]/dt = k_1([\mathrm{PBzN}] + [\mathrm{PBzN}^*])[^{15}NO_2]/([NO_2] + [^{15}NO_2]) \tag{12}$$

$\gg$ $[NO_2]$ and eq 12 reduces to eq 13. If the exchange reaction

$$d[\mathrm{PBzN}^*]/dt = -d[\mathrm{PBzN}]/dt = k_1([\mathrm{PBzN}] + [\mathrm{PBzN}^*]) \tag{13}$$

is faster than any other loss mechanism, the sum of [PBzN] + [PBzN*] at any time is equal to [PBzN] initially present. Under these conditions, the rate of loss of PBzN equals the rate of formation of PBzN* and the observed first-order rate constants for d[PBzN*]/dt and −d[PBzN]/dt will be equal to k_1. As with PAN,[45] we expected that the peroxynitrate $-NO_2$ stetching frequency at 1740 cm^{-1} would be common to both PBzN and PBzN*. The exchange reaction could thus be easily monitored by adding $^{15}NO_2$ to PBzN and repeatedly scanning the 1900–1600-cm^{-1} region of the spectrum. This experiment was performed for 4.51×10^{-7} M PBzN at 303.6 K in the presence of 7.66×10^{-6} M $^{15}NO_2$. From the IR absorbances at 1805, 1740, and 1700 cm^{-1}, it was clear that exchange between PBzN and $^{15}NO_2$ occurred to produce PBzN*.

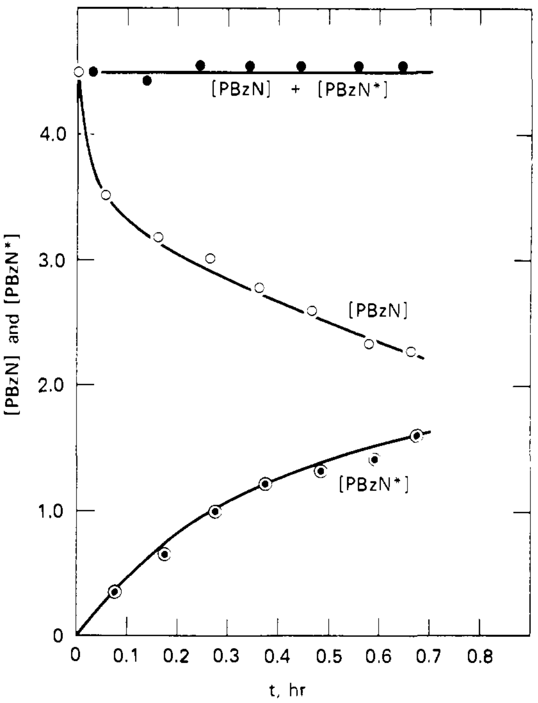

Figure 3. Concentrations of PBzN, PBzN*, and PBzN + PBzN* vs. time for reaction of 4.51×10^{-7} M PBzN with 1.85×10^{-6} M $^{15}NO_2$ (800 torr argon) at 303.6 K. Data of Table VI, run 3.

Table VI. Observed First-Order Rate Constants (k_{obsd})[a] for Disappearance of PBzN in the Presence of Added $^{15}NO_2$ at 303.6 K[b]

run no.	10^7-$[\mathrm{PBzN}]_0$, M	10^5-$[^{15}NO_2]_0$, M	$10^5 k_{\mathrm{obsd}}$, s^{-1}
1	4.99	1.23	40.1
2	5.77	4.36	31.3
3	4.73	1.85	19.9
4	4.60	2.33	29.6
5	5.08	2.33	39.6
6	5.81	5.59	20.0
		av	30.1 ± 0.84

[a] k_{obsd} calculated from the slope of the semilog plot of $[\mathrm{PBzN}]_t/[\mathrm{PBzN}]_0$ vs. time, where [PBzN] is determined from the absorbance at 1740 cm^{-1}. [b] All experiments were performed at 800 torr total pressure with Argon as diluent gas.

When using the published[38] extinction coefficients for PBzN, $\epsilon_{1805} = 1.69 \times 10^4$ M^{-1} m^{-1} and $\epsilon_{1740} = 5.57 \times 10^4$ M^{-1} m^{-1}, and assuming $\epsilon_{1700} = 5.57 \times 10^4$ M^{-1} m^{-1} for PBzN*, the changes in concentration of PBzN, PBzN*, and PBzN + PBzN* were monitored as a function of time. Data obtained in this manner are shown in Figure 3. From the figure, the decrease in PBzN and the concomitant increase in PBzN* are readily seen, as is the invariance in the concentration of PBzN plus PBzN*. A semilog plot (not shown) of $[\mathrm{PBzN}]_t/[\mathrm{PBzN}]_0$ is linear, with slope 19.9×10^{-5} s^{-1}, indicating first-order disappearance of PBzN. This experiment was run six times under various conditions, and for each run, a value of k_{obsd} was obtained for the disappearance of PBzN. These data are given in Table VI. For the six runs the average value $k_{\mathrm{obsd}} = (30.0 \pm 8.9) \times 10^{-5}$ s^{-1} is in excellent agreement with the values of k_{obsd} obtained for disappearance of PBzN in the presence of NO, $k = (36.2 \pm 3.3) \times 10^{-5}$ s^{-1}. Un-

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[43] L. Batt and R. T. Milne, *Int. J. Chem. Kinet.*, **9**, 549 (1977).

[44] K. R. Darnall, W. P. L. Carter, A. M. Winer, A. C. Lloyd, and J. N. Pitts, *J. Phys. Chem.*, **80**, 1948 (1976).

[45] E. L. Varetti and G. C. Pimentel, *Spectrochim. Acta, Part A*, **30**, 1069 (1974).

Table VII. Observed First-Order Rate Constants (k_{obsd})[a] for the Decomposition of PBzN at 303.6 K in the Presence of Added NO and NO_2

10^5-[PBzN]$_0$, M	10^5-[NO_2], M	10^5-[NO], M	10^5-k_{obsd},[b] s^{-1}	k_2/k_{-1}[c]
b	0	*b*	36.2	*b*
5.78	30.9	4.22	6.19	1.51
4.58	8.78	15.0	25.5	1.39
7.18	10.3	9.26	20.9	1.52
3.93	15.7	7.09	14.4	1.46
4.33	14.4	4.26	12.2	1.72
			av	1.52 ± 0.12

[a] k_{obsd} calculated from the slope of the semilog plot of $[\mathrm{PBzN}]_t/[\mathrm{PBzN}]_0$ vs. time. [b] Data of Table II, runs 11-15. [c] k_2/k_1 calculated from eq 16 using $k_1 = 36.2 \times 10^{-5}\ s^{-1}$, see text.

questionably, the only mechanism that satisfactorily accounts for identical rate constants for all these processes is PBzN homolysis via reaction 1. We thus consider the mechanism for PBzN to be established conclusively.

Competitive Reactions of $C_6H_5C(O)OO\cdot$ with NO and NO_2. Having established the mechanism for disappearance of PBzN, we wished to take advantage of the equilibrium 1,–1 and reaction 2 to determine the relative rate constants for reaction of benzoylperoxy radicals with NO_2 (k_{-1}) and with NO (k_2). These processes are important insofar as the ratio $k_{-1}[NO_2]/k_2[NO]$ will determine the fate of PBzN in the environment.[46] Under conditions when $[NO_2]/[NO]$ is typically high (e.g., at night), PBzN may be relatively stable, but when $[NO_2]/[NO]$ is low (e.g., in the morning hours when auto emissions increase) PBzN decomposition can occur. To determine the ratio k_{-1}/k_2, we observed the rate of PBzN decomposition at 303.6 K in the presence of NO_2 and NO added in comparable amounts. Under these conditions, eq 8 applies. Taking the reciprocal of eq 8 and rearranging gives

$$k_{\mathrm{obsd}}^{-1} = (k_1)^{-1} + (k_{-1}/k_1k_2)[NO_2]/[NO] \qquad (14)$$

Providing that both NO_2 and NO are added in excess of the initial [PBzN], the disappearance of PBzN will be first order in [PBzN] and the observed first-order rate constant can be determined from a semilog plot of $[\mathrm{PBzN}]_t/[\mathrm{PBzN}]_0$ vs. time. In these experiments, the semilog plots were linear to as much as 85% decomposition. Values of k_{obsd} obtained in this manner are listed in Table VII, along with reaction conditions used. With use of the value of $k_1 = 36 \times 10^{-5}\ s^{-1}$ taken from the data of Table II, the ratio of k_2/k_{-1} was calculated for each run from the expression

$$k_2/k_{-1} = [NO_2]/k_1[NO](k_{\mathrm{obsd}}^{-1} - k_1^{-1})^{-1} \qquad (15)$$

The ratio $k_2/k_{-1} = 1.52 \pm 0.12$ at 303.6 K can be compared to our earlier value for PAN, where $k_2/k_{-1} = 3.02 \pm 0.68$ (independent of temperature) and to the value of $k_2/k_{-1} = 1.8 \pm 0.6$ as determined for PAN by Cox and Roffey.[30] Thus, according to our data the acetylperoxy and benzoylperoxy radicals differ by a factor of nearly 2 in terms of the relative rates of reaction with NO and NO_2. The absolute values for k_{-1} and k_2 can be estimated if we assume that reaction -1 proceeds with zero activation energy. In this case

$$k_{-1} = A_{-1} \qquad (16)$$

From transition-state theory[42]

$$A_1/A_{-1} = \exp(\Delta S_{-1}{}^{\circ}/R) \qquad (17)$$

Since $\Delta S_{-1}{}^{\circ} \simeq 30$ cal deg^{-1}, $k_{-1} \simeq 1 \times 10^9\ M^{-1}\ s^{-1}$; then from $k_2/k_{-1} = 1.52$, $k_2 \simeq 1.5 \times 10^9\ M^{-1}\ s^{-1}$.

Conclusions

PBzN is seen to be typical of all peroxynitrates studied to date in that O–N cleavage is the predominant mechanism for homolysis. At 303 K, the ratio of rate constants for O–N/O–O homolysis is at least 27. This ratio is regarded as a lower limit, since under our conditions surface effects may enhance the rate of PBzN decomposition in the absence ofNO as a radical scavenger. Based on the activation parameters for O–N homolysis, $k_1 = 10^{(15.2\pm0.60)}e^{(-25900\pm910/RT)}$, PBzN will be more stable than PAN at a given temperature. With respect to the environment, the stability of PBzN relative to PAN will be further increased because PBzN is less strongly dependent on the $[NO]/[NO_2]$ ratio ($k_2/k_{-1} = 1.5$) than is PAN ($k_2/k_{-1} = 3.0$). This analysis suggests that PBzN will be less effective than PAN in initiating radical chains via reactions 1 and 2 but than PBzN will be more prone to accumulate in the environment, thereby retarding the overall chemistry. Since the peroxyaroyl nitrates are more potent lachrymators than PAN, the dual effects of increased stability and increased biological activity could make peroxyaroyl nitrates potentially more important in contributing to eye irritation than peroxyacyl nitrates if both types of peroxynitrates are formed in comparable amounts.

Finally, because the dissociation of PBzN is temperature dependent, it is likely that peroxyaroyl nitrates like peroxyacyl nitrates contribute significantly to the temperature dependence of photochemical smog formation.

Experimental Section

Materials. Peroxybenzoyl nitrate was prepared by reaction of peroxybenzoic acid[47] with NO_2BF_4 in pentane solvent. This is a slight modification of the method of Louw et al.,[10] who used HNO_3/H_2SO_4 or N_2O_5 as the nitrating agent. PBzN was identified by its characteristic IR spectrum. NO, NO_2, and argon were supplied by Matheson Gas Co., whereas $^{15}NO_2$ was obtained from Stohler Isotope Co. $^{15}NO_2$ and NO_2 were purified by reaction with O_2; NO was purified by passing the gas over 13X mole sieves and then through a cold trap cooled with liquid oxygen.

Apparatus. All experiments were performed in a Wilkes Scientific variable path length IR cell with a path length of 0.75 to 21.75 m. We typically used a path length of 15.75 m in our experiments. The cell body is made of Monel steel; gold and stainless steel fittings are used throughout. AgBr cell windows were used. A Forma Scientific Model 2095 constant temperature circulating bath was used to circulate water through coils wrapped around the exterior of the cell and covered with fiberglass insulation. The temperature of the water was controlled to within ±0.1 K, although temperature variations in the cell were probably as high as ±0.5 K at the highest temperatures used because of heat exchange through the upper and lower surfaces of the cell. A Perkin-Elmer Model 457 infrared spectrophotometer was used in conjunction with an external strip chart recorder to monitor changes in the IR spectra. Reactant pressures were determined using a calibrated Validyne Model DP7 transducer, and argon pressure in the cell was determined with a Wallace and Tiernan pressure gauge.

Procedures. For PBzN decompositions in the absence of added reactants, PBzN was first added to the evacuated cell via syringe. Then argon was added to 800 torr, and the absorbance at 980 cm^{-1} was recorded as a function of time. When NO, NO_2, $^{15}NO_2$, or mixtures of NO plus NO_2 were used, the procedures were as follows. PBzN was added to the evacuated cell, and reactants were added at a given pressure to a 258-mL glass bulb fitted with stopcocks on either end. The 258-mL bulb was then connected to the IR cell, the contents of the bulb were swept into the cell with a stream of argon, and the final concentration of reactant in the system was calculated on the basis of the cell volume (3.4 L). The NO_2/N_2O_4 equilibrium[48] was taken into account in all calculations. PBzN disappearance was monitored at 980 cm^{-1} for reactions in the presence of NO, NO_2, and NO plus NO_2. For the exchange reaction with $^{15}NO_2$, the 1900–1600-cm^{-1} region of the spectrum was scanned and the output was recorded on a continously moving strip chart. Absorbances of 1805, 1740, and 1700 cm^{-1} could thus be determined at any time.

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Registry No. PBzN, 6786-32-9.

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[46] D. G. Hendry and R. A. Kenley, in "Nitrogenous Air Pollutants", D. Grosjean, Ed., Ann Arbor Science, Ann Arbor, Mich., **1979**.

[47] D. Swern in "Organic Peroxides", Vol I, D. Swern, Ed., Wiley-Interscience, New York, 1970.

[48] D. Gray and A. D. Yoffe, *Chem. Ref.*, **55**, 1069 (1955).