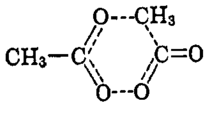
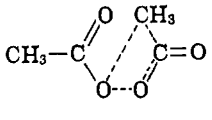
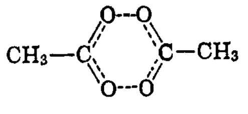
law for scrambling of label to rule out mechanisms involving intermolecular exchange with traces of acetic acid formed in the reaction.

The intramolecular nature[1,2] of the reaction leading to ethane and methyl acetate was confirmed in this work by failure to observe more than 0.1% of trideuterio cross-product in the ethane and methyl acetate formed in the decomposition of an equimolar mixture of ordinary diacetyl peroxide and diacetyl-$d_6$ peroxide. Methyl acetate (containing the equivalent of 0.627% excess oxygen-18 in one oxygen), formed directly in the decomposition of the peroxide (0.630% label in the carbonyl oxygen), showed complete scrambling of label. This was determined by lithium aluminum hydride reduction to give methanol (0.314% excess, 50.0% of the total label) and ethanol (0.312% excess, 49.8% of the label) with equivalent label, thus ruling out the operation of cyclic mechanisms A or B for the intramolecular route leading to this product. The analogous mechanism, C, for scrambling of label in recovered peroxide cannot definitely be ruled out until the results of double labeling experiments are in hand.

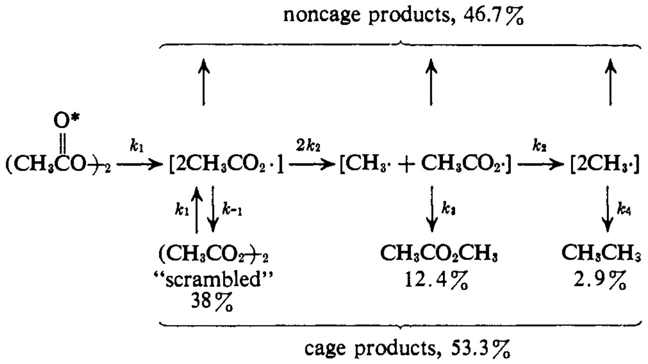

A


B


C

It should be noted that the cage return of acetoxy radicals to give acetyl peroxide to the extent here indicated provides a competition between decarboxylation ($2k_2$, expected to show a $^{13}$C kinetic isotope effect) and recombination ($k_{-1}$, showing only a secondary kinetic isotope effect). This provides an alternative basis for explaining the over-all kinetic isotope effect reported[8] for carboxy carbon-13 in the decomposition of the peroxide. It is clear that in the limiting case with $k_{-1} >> 2k_2$ the apparent kinetic isotope effect will approach that for the decarboxylation of acetoxy radical. Our observations suggest that $k_{-1}$ is at least comparable with $2k_2$. It is therefore possible to approach the task of explaining the observed[8] kinetic isotope effect without postulating multiple bond cleavage, leading directly to methyl radicals from acetyl peroxide,[8] as an important pathway in the decomposition scheme.[9]

Diacyl peroxides which on decarboxylation lead to *sec*-alkyl radicals have been shown[10] to decompose *via* the carboxy inversion route. The methyl ester of the mixed carbonic–acetic anhydride has been shown,[11] however, to be too stable to serve as an intermediate in the decomposition of acetyl peroxide.



All of the data now available seem to be consistent with the simple O–O bond cleavage of acetyl peroxide, followed by cage reactions of the two initially formed acetoxy radicals which are competitive with decarboxylation and diffusion from the cage.

The cage recombination of acetoxy radicals may also explain the monotonic decrease in over-all rate of decomposition observed[3] for acetyl peroxide with increasing solvent viscosity and account for its faster decomposition in the gas phase. Rate comparisons from the work of Herk, Feld, and Szwarc[2] suggest $k_{\text{gas}}/k_{\text{isooctane}} = 1.55$ at 80°, compared with a ratio of 1.61 calculated from our data, equating cage return to scrambling of label, and assuming the cage effect to be the only solvent effect on rate. While the close agreement must be considered fortuitous, this result makes it seem unlikely that a large amount of cage return occurs without scrambling of label.

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(8) M. J. Goldstein, *Tetrahedron Letters*, 1601 (1964), reports $k_{12}/k_{13} = 1.023$ (45°) as reflected in the isotopic composition of the initially evolved carbon dioxide.

(9) T. W. Koenig and W. D. Brewer, *ibid.*, 2773 (1965), arrive at the same conclusion on the basis that they observe essentially no secondary kinetic isotope effect in the decomposition of diacetyl-$d_6$ peroxide. Rationalization of this result in terms of our findings must await further work. We note a small $^{13}$C kinetic isotope effect (1.005–1.010) reflected in the isotopic composition of methane generated from decomposition of acetyl peroxide in isooctane, 80°.

(10) F. D. Greene, H. A. Stein, C. C. Chu, and M. Vane, *J. Am. Chem. Soc.*, **86**, 2080 (1964).

(11) F. D. Greene, private communication.

(12) Rohm and Haas Company Fellow, 1962–1963; National Institutes of Health Predoctoral Fellow, 1963–1964.

(13) Fellow of the Alfred P. Sloan Foundation.

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*Received May 16, 1966*

## Deuterium Isotope Effect in Amine-Catalyzed Aromatic Nucleophilic Substitution. The Reaction of 4-Chloro-3-nitrobenzotrifluoride with Piperidine and N-Deuteriopiperidine in Benzene

*Sir:*

In reactions of halonitrobenzenes with amines the over-all second-order rate coefficient $k_T$ generally increases with the initial amine concentration, and this kinetic order, higher than one with respect to the nucleophile, is consistent with the base-catalyzed mechanism (I), studied by Ross,[1] Bunnett,[2-4] and others.[5-10]

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(1) S. D. Ross, *Progr. Phys. Org. Chem.* 1, 31 (1963).

(2) J. F. Bunnett and J. J. Randall, *J. Am. Chem. Soc.*, **80**, 6020 (1958).

(3) J. F. Bunnett and R. H. Garst, *ibid.*, 87, 3875 (1965).

(4) J. F. Bunnett and R. H. Garst, *ibid.*, 87, 3879 (1965).

(5) N. E. Sbarbati, T. H. Suarez and J. A. Brieux, *Chem. Ind.* (London), 1754 (1964).

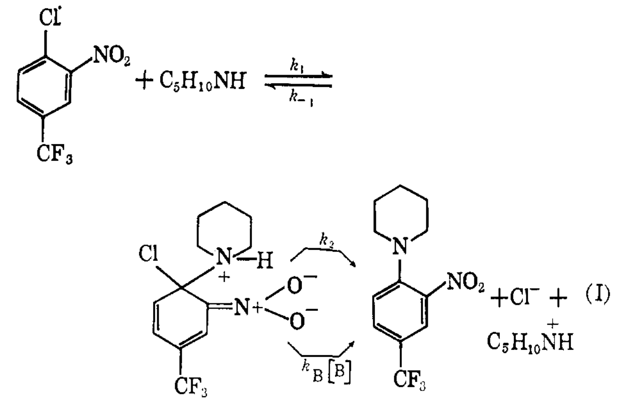
(6) O. L. Brady and F. R. Cropper, *J. Chem. Soc.*, 507 (1950).

(7) F. Pietra and A. Fava, *Tetrahedron Letters*, 1535 (1963).

(8) H. Suhr, *Ber. Bunsenges Physik. Chem.*, 67, 893 (1963).

(9) H. Zollinger and C. Bernasconi, *Tetrahedron Letters*, 1083 (1965).

(10) F. Pietra, *ibid.*, 2405 (1965).



Hence, if the heterolysis of the N–H bond were the rate-determining step, a deuterium isotope effect should be observable when deuterated amines are employed. This effect on $k_T$ values has in fact been observed,[10,11] but its absence has also been reported.[7,9,12,13]

We now report the reactions of 4-chloro-3-nitrobenzotrifluoride with piperidine and N-deuteriopiperidine in benzene at 35°; these reactions show an over-all isotope effect $k_T(H)/k_T(D) = 1.2$ (piperidine and N-deuteriopiperidine 0.25 *M*). As could be expected, the isotope effect is mainly associated with variations in $k_B$ values (see Table I and Figure 1).

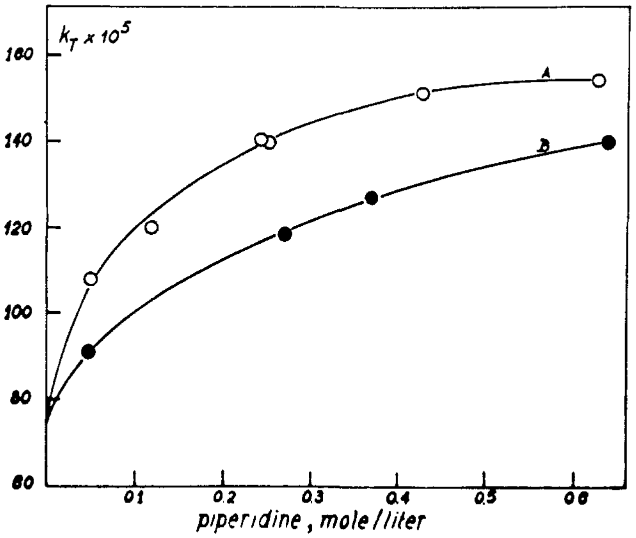


Figure 1. Second-order rate coefficients for the reaction of piperidine and N-deuteriopiperidine with 4-chloro-3-nitrobenzotrifluoride, as a function of nucleophile concentration (data of Table I): A, with piperidine; B, with N-deuteriopiperidine.

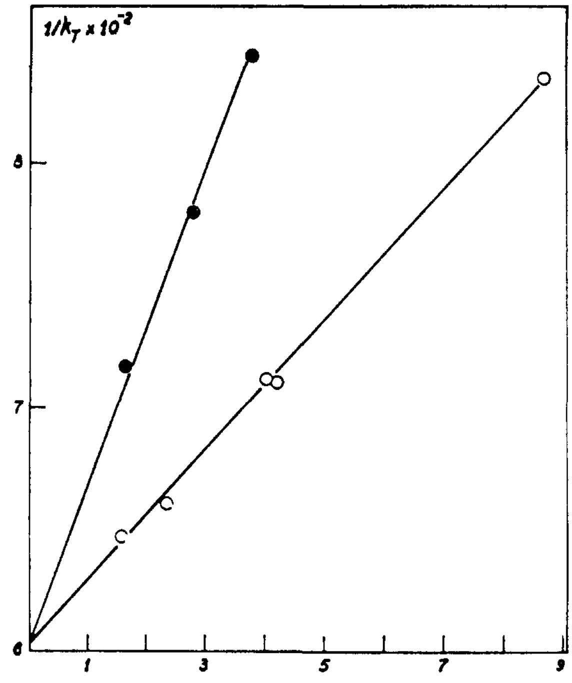


Figure 2. Plot of $1/k_T$ *vs.* 1/[B] calculated from the data of Table I: A, with piperidine; B, with N-deuteriopiperidine. For convenience in plotting, the 0.05 *M* nucleophile points are omitted.

Table I shows the experimental data and related kinetic parameters. Plotting $k_T$ values, obtained at constant initial substrate concentration (0.1 ± 0.001 *M*), against variable initial amine concentrations, curves A and B of Figure 1 are obtained for piperidine and N-deuteriopiperidine, respectively. The form of curve A agrees with eq i obtained by applying steady-state theory to mechanism I and, according to Bunnett's views,[3] it can be considered strong support for catalysis by piperidine.

$$k_T = \frac{k_1k_2 + k_1k_B[B]}{k_{-1} + k_2 + k_B[B]} \qquad \text{(i)}$$

Table I includes derived $k_1$, $k_2/k_{-1}$, and $k_B/k_{-1}$ values for both reactions, calculated as suggested by Bunnett.[3] The reciprocal plots, $1/k_T$ *vs.* 1/[B], are linear (Figure 2), having a common origin $1/k_1$ and different slopes $k_{-1}/k_1k_B$. The points for 0.05 *M* piperidine and 0.05 *M* N-deuteriopiperidine concentrations fall

**Table I.** Over-all Rates, $k_T$, for Reactions of 4-Chloro-3-nitrobenzotrifluoride with Piperidine and N-Deuteriopiperidine at 35° and Related Kinetic Parameters

| Substrate, *M* | Nucleophile, *M* | $10^5k_T$, l. mole$^{-1}$ sec$^{-1}$ |
|---|---|---|
| | $C_5H_{10}NH$ | |
| 0.1103 | 0.0539 | 108.0 |
| 0.1103 | 0.1170 | 119.7 |
| 0.1104 | 0.2417 | 140.7 |
| 0.1101 | 0.2519 | 140.0 |
| 0.1102 | 0.4280 | 151.3 |
| 0.1096 | 0.6283 | 154.2 |
| $10^5k_1$ = 166.2 l. mole$^{-1}$ sec$^{-1}$; $k_B/k_{-1}$ = 22.0 l. mole$^{-1}$; $k_2/k_{-1}$ = 0.76 | | |
| | $C_5H_{10}ND^a$ | |
| 0.1104 | 0.0489 | 90.8 |
| 0.1100 | 0.2705 | 118.5 |
| 0.1101 | 0.3587 | 128.0 |
| 0.1100 | 0.6416 | 139.5 |
| $10^5k_1$ = 160.7 l. mole$^{-1}$ sec$^{-1}$; $k_B/k_{-1}$ = 10.5 l. mole$^{-1}$; $k_2/k_{-1}$ = 0.73 | | |

[a] Approximately 70% $C_5H_{10}ND$ was used as estimated by nmr spectra and supported by mass and infrared spectral evidence.

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(11) H. Zollinger, *Ann. Rev. Phys. Chem.*, 13, 405 (1962).

(12) M. F. Hawthorne, *J. Am. Chem. Soc.*, 76, 6358 (1954).

(13) S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, 81, 5336 (1959).

below the lines established by the rest of the points. These expected deviations are also consistent with eq i.[3] From the slopes, intercepts, and $k_T$ values for 0.05 $M$ nucleophile concentration, the ratios $k_2/k_{-1}$ are calculated to be the same. Hence the autodecomposition of the intermediate to yield the products or backwards to yield the reactants is an intrinsic property not influenced by the nucleophile concentration or by the attachment of a proton or a deuteron to the nucleophile.

The constancy of $k_1$ and $k_2/k_{-1}$ values as well as the ratio $k_{B(H)}/k_{B(D)}$ = 2.1 suggest that the proposed mechanism is very likely correct. The rate-determining step would be the heterolysis of the N-H bond in the catalyzed pathway. These results suggest that a deuterium isotope effect in aromatic nucleophilic substitutions must be studied using a broad range of nucleophile concentration. Failure in this requirement would explain the reported absence[7,9,12,13] of a kinetic isotope effect in several similar reactions.

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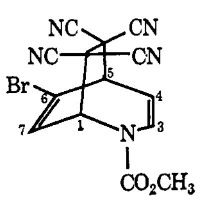
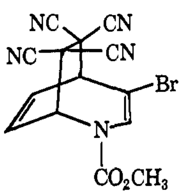
## Structure of Cocrystallized Cycloadducts from 3- and 4-Bromo-N-carbomethoxyazepine and Tetracyanoethylene[1,2]

*Sir:*

The cycloadducts from N-carboxyazepines and tetracyanoethylene have recently been shown[3-5] to result from Diels–Alder reactions, rather than from 2,6 cycloadditions.[6] The monosubstituted azepines derived from monosubstituted benzenes and carbomethoxynitrene gave adducts with tetracyanoethylene identified primarily through nmr spectroscopy as 6-substituted 8,8,9,9-tetracyano-2-carbomethoxy-2-azabicyclo[3.2.2]nona-3,6-dienes[3] (*e.g.*, I). To confirm these



I



II

assignments and to determine the detailed stereochemical structure of a representative cycloadduct in this class, an X-ray single crystal structure analysis of the solid, thought to be I, was undertaken.

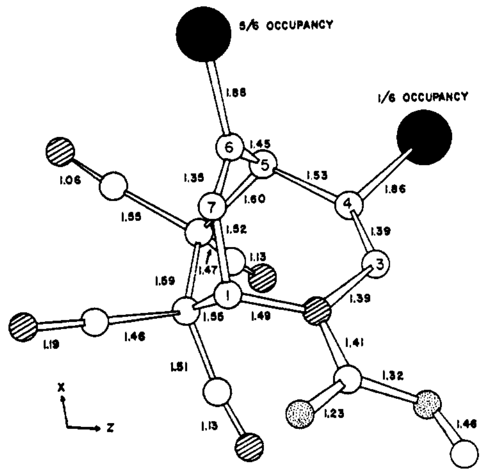


Figure 1. Stereographic view of the cocrystallized molecules I and II along the $y$ axis. The standard deviation of a typical C–C bond is 0.028 A.

The crystals of the adduct (mp 163–167°, recrystallized five times from toluene[7]) belong to the monoclinic system with $a$ = 19.25 ± 0.03, $b$ = 10.87 ± 0.02, $c$ = 8.98 ± 0.02 A, and $\beta$ = 101° 30′ ± 15′. The cell parameters were measured from precession photographs (Mo K$\alpha$, $\lambda$ 0.7107 A). The space group is $P2_1/a$ and there are four molecules of $C_{14}H_8O_2N_5Br \cdot 0.5C_7H_8$ in the unit cell; the measured density is 1.49 g/cc compared to the calculated value of 1.46 g/cc. A total of 1605 independent structure amplitudes was recorded visually from equiinclination Weissenberg photographs (Cu K$\alpha$, $\lambda$ 1.5418 A) taken at 3°. The signs of the structure amplitudes were obtained by the heavy-atom method[8] and the molecular structure was shown to be consistent with I. Refinement proceeded to a crystallographic $R$ factor of 0.18, and the calculated distances and angles were in fair agreement with expected values.

It proved impossible, however, to refine the structure beyond this point by least-squares techniques. Furthermore, in the course of the refinement, the temperature factors associated with most of the carbon, nitrogen, and oxygen atoms tended to assume negative values, which correspond to a physically unreal situation. Computation of a difference map at this stage revealed peaks around two of the crystallographic centers of symmetry corresponding to a disordered orientation for the toluene molecules, which had been previously undetected, and an unexpected peak situated approximately 1.9 A from C(4). The density of this peak was close to that expected for a carbon or oxygen atom. With this peak included as a carbon atom in further refinements, the $R$ factor and the sum of the least-squares residuals were successfully reduced. The unexpected peak, however, remained about 1.90 A from C(4) and subtended reasonable bond angles be-

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(1) This work was supported in part by the National Science Foundation (GP-5226) and the National Institutes of Health (GM 12470-02 and 5T1 GM 722-05).

(2) Cycloadditions. VII. Paper VI: J. E. Baldwin and J. P. Nelson, *J. Org. Chem.*, 31, 336 (1966).

(3) J. E. Baldwin and R. A. Smith, *J. Am. Chem. Soc.*, 87, 4819 (1965).

(4) J. H. van den Hende and A. S. Kende, *Chem. Commun.*, 384 (1965).

(5) A. S. Kende, P. T. Izzo, and J. E. Lancaster, *J. Am. Chem. Soc.*, 87, 5044 (1965).

(6) K. Hafner, *Angew. Chem.*, 75, 1041 (1963); *Angew. Chem. Intern. Ed. Engl.*, 3, 165 (1964).

(7) Analytical data for material prepared by thorough pumping had corresponded to $C_{14}H_8O_2N_5Br$.[3] In the course of the present investigation, an elemental analysis on the crystals being used in the X-ray work indicated the presence of toluene of crystallization, corresponding to $C_{14}H_8O_2N_5Br \cdot 0.5C_7H_8$. Complete removal of toluene afforded material which melted sharply at 167–169°, but which was unsuitable for single crystal studies.

(8) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 219 (1937).