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THE SOLVOLYSIS OF BENZHYDRYL p-NITROBENZOATE-CARBONYL-^{18}O

A NEW METHOD FOR DETECTING ION PAIR RETURN

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RECENTLY[2] it was discovered that in the trans-5-methyl-2-cyclohexenyl p-nitrobenzoate system internal return results in equilibration of the carboxyl oxygen atoms at a rate greater than that of allylic rearrangement (racemization). This suggested that equilibration of carboxyl oxygen atoms might be a useful method for detecting ion pair return in systems which do not rearrange. This possibility had been investigated earlier with negative results - ether-^{18}O 2,4-dimethylhex-4-yl acid phthalate remains discretely labelled during solvolysis.[3]

We have now examined the solvolysis of carbonyl-^{18}O benzhydryl p-nitrobenzoate in 90% aqueous acetone and have found that the carboxyl oxygen atoms are indeed equilibrated during solvolysis. At 118.6° both solvolysis (followed titrimetrically) and oxygen equilibration are first-order.

The overall process can be summarized as follows.

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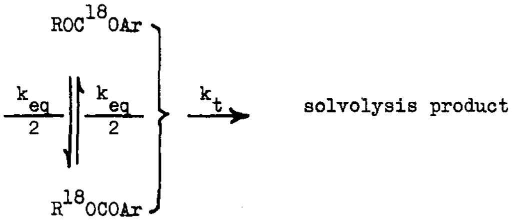
[1] National Science Foundation Fellow.

[2] H.L. Goering and J.T. Doi, J.Amer.Chem.Soc. 82, 5850 (1960).

[3] W.E. Doering, A. Streitwieser, Jr. and L. Friedman, Unpublished work cited by A. Streitwieser, Jr., Chem.Rev. 56, 663 (1956).



The first-order rate constant for equilibration of the carboxyl oxygen atoms in the unsolvolyzed ester [k_{eq}, equation (1)] is 18.7 x $10^{-3}hr^{-1}$. This reaction was followed by starting with ^{18}O-carbonyl-labelled ester and determining the ^{18}O distribution in the remaining ester at appropriate time intervals. The first-order rate constant for solvolysis, k_t, is 6.4 x 10^{-3} hr^{-1}[4] which is three times smaller than k_{eq}. From the high solvolytic reactivity it is clear that solvolysis involves alkyl-oxygen cleavage.[5]

$$ROC^{18}OAr \xrightarrow{k_{eq}} R^{18}OC^{18}OAr \tag{1}$$

Since the first-order rates of solvolysis (followed to 75% completion) and oxygen equilibration (followed to 85% completion) are steady, except for the upward trend in k_t in experiments without added solutes,[4] it is apparent that equilibration must be largely intramolecular--equilibration at the observed rate by a dissociation-recombination mechanism (external

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[4] There is a rather large positive salt effect for solvolysis; k_t is increased about 20% by 0.042 M p-nitrobenzoic acid and 80% by 0.045 M lithium p-nitrobenzoate. Because of the salt effect k_t shows an upward trend in experiments without added solutes, e.g. the integrated constants drift from 5.7 x $10^{-3}hr^{-1}$ (12% reaction) to 6.6 x $10^{-3}hr^{-1}$ (75% reaction) and the initial rate constant, obtained by extrapolation, is about 5.5 x $10^{-3}hr^{-1}$. In experiments with added p-nitrobenzoic acid (0.015 to 0.043 M) good first-order behavior was observed.

[5] For additional evidence bearing on this point see M.S. Silver, J.Amer.Chem.Soc. **83**, 404 (1961).

return) would require considerable drifts in both k_t (downward) and k_{eq} (upward).

The intramolecular nature of the oxygen equilibration process was established by an independent method. The rate at which the unsolvolyzed ester exchanges with p-nitrobenzoic acid under conditions of the solvolysis (and oxygen equilibration) was established using ^{14}C-labelled p-nitrobenzoic acid. This rate was found to be first-order in both ester and p-nitrobenzoic acid; the second-order constant is 2.0×10^{-2} l. mole^{-1}hr^{-1}. From this exchange constant, and the average p-nitrobenzoic acid concentration in the medium, the fraction of ester that will undergo exchange during any period can be computed. Under the conditions of the oxygen equilibration experiments the only p-nitrobenzoic acid present is that formed by solvolysis. From the rate of exchange between ester and p-nitrobenzoic acid it can be shown that under these conditions after 103 hr (86% equilibration of oxygen atoms) only 2.5% of the remaining ester will have undergone exchange. Clearly the oxygen equilibration process is essentially completely intramolecular in the sense that the alkyl group remains attached to the same carboxyl group.

Presumably the intromolecular oxygen-equilibration process which accompanies solvolysis involves ion pair return (probably internal return).[6,7] If the oxygen atoms in the intermediate ion pair (I) are equivalent, the rate constant for ionization (k_1) is ($k_{eq} + k_t$) and the rate constant for formation of that fraction of I which returns to substrate is k_{eq}. However,

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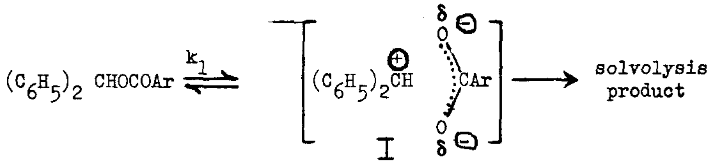
[6] S. Winstein, E. Clippinger, A.H. Fainberg, R. Heck and G.C. Robinson, J.Amer.Chem.Soc. **78**, 328 (1956).

[7] It was shown earlier[2] that the rate of oxygen equilibration without rearrangement in an allylic system is sensitive to the ionizing power of the solvent which is consistent with the idea that the process involves internal return.

the oxygen atoms in I may not be completely equivalent and thus rates of ionization determined by this method are lower limits. Presumably the dissociated carbonium ion is an intermediate in the solvolysis-product forming step.



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If the present interpretation is correct, equilibration of carboxyl oxygen atoms is an important method for detecting ion pair return because it is applicable in systems which do not rearrange. Moreover, optically active systems are not required. Except for detection of ion pair return by an "abnormal" salt effect[8] (which does not reveal internal return) methods used previously[9] are applicable only in systems which racemize or rearrange.[10]

Preliminary experiments[12] with optically active *p*-chlorobenzhydryl *p*-nitrobenzoate indicate that the intramolecular oxygen equilibration process is largely but not completely stereospecific (retention).[13]

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[8] S. Winstein, P.E. Klinedinst, Jr. and G.C. Robinson, J.Amer.Chem.Soc. 83, 885 (1961).

[9] For leading references see H.L. Goering, Rec.Chem.Progr. 21, 109 (1960).

[10] An important method for detecting ion pair return associated with the ionization of substituted benzhydryl chlorides has recently been developed by Winstein and coworkers.[11] This method involves comparison of rates of racemization and radio-chloride exchange and is applicable to systems which do not rearrange. However, optically active systems are required. Moreover, unlike with the present method, return with retention of configuration is not detected.

[11] S. Winstein, J.S. Gall, M. Hojo and S. Smith, J.Amer.Chem.Soc. 82, 1010 (1960); S. Winstein and J.S. Gall, Tetrahedron Letters No. 2, 31 (1960); S. Winstein, M. Hojo and S. Smith, Ibid. No. 22, 12 (1960); Y. Pocker, Proc.Chem.Soc. 140 (1961).

[12] Unpublished work by R.G. Briody.

[13] In ref. 2 it was reported that oxygen equilibration without rearrangement is stereospecific (retention) in a cyclic allylic system.