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The Stereochemistry of the Replacement of Chlorine Atoms in Alkyl Halides by Chlorine-38 Activated in the (n,γ) Process¹

Sir:

Radioactive halogen species formed by the (n,γ) nuclear reaction were the subjects of most of the initial studies of hot atom chemistry² and have been extensively studied since.^{3,4} The observation of organic "retention" of radioactivity following neutron irradiation is an example of the formal replacement of the halogen atom in an alkyl halide by a radioactive halogen, as in eq. 1.³⁻⁵



The observation of this reaction inspired the early "billiard-ball" theory of hot atom reactions,⁶ and its understanding is of fundamental importance to the recoil chemistry of the halogens.

Despite the large number of experiments reported previously for various halogen isotopes, no information has been available on the stereochemistry of reaction 1.⁷ Complete resolution of a racemic mixture into pure *d* and *l* components in 1 or 2 hr. was not an inviting prospect, so our experiments were conducted with chlorinated molecules containing two asymmetric carbon atoms, the *meso* and *dl* forms of 2,3-dichlorobutane. The *meso* and *dl* forms can be readily separated from one another by gas chromatography, utilizing a 15-ft. column of tritoyl phosphate on firebrick, operated at 100° (retention times: *meso*, 62 min.; *dl*, 73 min.). The halogen isotope studied was Cl³⁸ ($t_{1/2}$ = 37 min.) created by the (n,γ) reaction on the Cl³⁷ isotope contained in the target molecule.

The *meso* and *dl* forms of 2,3-dichlorobutane were prepared by the low temperature addition of Cl₂ to the *cis* and *trans* forms of butene-2, respectively.⁸ The original preparations were 99% (*meso*) and 95% (*dl*) stereospecific, and needed no further purification after the first experiments showed the trend of the results. Irradiation of *meso*-2,3-dichlorobutane in the liquid phase at 20° results in the formation of Cl³⁸

labeled *meso*- and *dl*-2,3-dichlorobutane in the approximate ratio 1.0:0.39 ± 0.02, as shown in Table I. Experiments with *dl*-2,3-dichlorobutane showed a similar 1.0:0.40 ± 0.02 ratio of Cl³⁸ labeled target molecule to labeled diastereomer. Both the absolute yields of the labeled diastereomers and their yield ratio were essentially unaffected by the presence or absence of free-radical scavengers. The absolute yields in per cent of total Cl³⁸ are in the 3-10% range observed previously for RCl³⁸ from RCl in a variety of systems.^{3,9}

TABLE I

YIELDS OF Cl³⁸-2,3-DICHLOROBUTANES FROM (n,γ) REACTION ON *meso*- OR *dl*-2,3-DICHLOROBUTANE

Conditions Phase, temp. (°C.), scavenger	Relative yield ^a Cl ³⁸ - <i>meso</i> /Cl ³⁸ - <i>dl</i>
Target: <i>dl</i> -2,3-Dichlorobutane	
Liquid, 20, none	0.41 ± 0.02
Liquid, 20, DPPH ^b	0.38 ± 0.02
Liquid, 20, I ₂ ^c	0.36 ± 0.04
Liquid, -56, DPPH	0.65 ± 0.02
Solid -78, none	0.95 ± 0.03
Solid -78 ^d	0.99 ± 0.02
Solid -114 ^d	1.00 ± 0.03
Phase, temp., scavenger	
Target: <i>meso</i> -2,3-Dichlorobutane	
Liquid, 20, none	0.41 ± 0.02
Liquid, 20, DPPH	0.36 ± 0.02
Liquid, 20, I ₂ ^c	0.44 ± 0.04
Liquid, -78, none	0.51 ± 0.02
Liquid, -78, DPPH	0.54 ± 0.03
Solid, -114 ^d	0.64 ± 0.02
Solid, est. -190 ^d	0.67 ± 0.02

^a Corrected for diastereomer purity and radioactive decay.

^b DPPH = diphenylpicrylhydrazyl. ^c The I₂-scavenged runs are not included in the average in the text because of the formation of large quantities of I¹²⁸ species which create a very high counter background during the passage of the Cl³⁸ peaks. ^d DPPH was present, but no information was obtained about the phase behavior of the solid binary mixtures.

When either of the 2,3-dichlorobutanes was irradiated in the gas phase (2 cm. pressure), the Cl³⁸ activity was reduced by a factor of 15-20 in the irradiated molecule from that observed in the liquid phase, and was zero within the limits of error in the diastereomer. The large increase in the radioactivity of the parent molecule between gas and liquid phases is consistent with previous observations.^{3,9} The chemical origin of the small fraction found as the radioactive parent molecule in the gas phase is uncertain, since γ -ray cancellation can very occasionally leave the original C-Cl bond unruptured.¹⁰

Prior to the experiments, three simple results seemed possible: (a) complete retention of configuration during substitution, as in recoil tritium substitution of T for H; (b) complete inversion, in analogy with the substitution of X⁻ into RX^{11,12}; and (c) complete racemization from the combination of Cl³⁸ with a racemized CH₃CHClCH₂ radical. None of these simple explanations can account by itself for the experimental

(9) J. E. Quinlan, Ph.D. Thesis, University of Wisconsin, 1958.

(10) Experiments by A. A. Gordus and C. Hsiung [*J. Chem. Phys.*, **36**, 955 (1962)] have shown that the original bonds survive the nuclear reaction and recoil in 0.1-0.5% of the activated molecules in the gas phase for Br and I radioactivities.

(11) E. D. Hughes, F. Juliusberger, S. Masterson, B. Topley, and J. Weiss, *J. Chem. Soc.*, 1525 (1935).

(12) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963.

(1) This research has been supported by A.E.C. Contract No. AT-(11-1)-407.

(2) L. Szilard and T. A. Chalmers, *Nature*, **134**, 462, 494 (1934).

(3) J. E. Willard, "Chemical Effects of Nuclear Transformations," Vol. 1, International Atomic Energy Agency, Vienna, 1961, p. 215.

(4) I. G. Campbell, "Advances in Inorganic and Radiochemistry," Vol. 5, Academic Press, Inc., New York, N. Y., p. 135.

(5) The charge states involved in reaction 1 are not unequivocally known, and no implication is intended that the reacting species is necessarily uncharged (see ref. 3).

(6) W. F. Libby, *J. Am. Chem. Soc.*, **62**, 1930 (1940); **69**, 2523 (1947).

(7) The stereochemistry of the replacement of H by recoil T has been investigated in several experiments with the consistent result that the substitution is accompanied by retention of configuration at an asymmetric carbon atom. See M. Henchman and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2991 (1961), for the gas phase results with *sec*-butyl alcohol; and J. G. Kay, R. P. Malsan, and F. S. Rowland, *ibid.*, **81**, 5050 (1959), for experiments with crystalline L-(+)-alanine.

(8) H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941).

observation. The most significant result for hot atom chemistry is the formation of *both* labeled molecules as products, indicative of a complex reaction mechanism involving the combination of two species to form the labeled product.

The differences in the organic yields for gas and liquid phase experiments with alkyl halides have been discussed in terms of the effect of the solvent "cage" in holding two reactive species in the near vicinity of one another until combination can occur, and in terms of the presence of a "brush heap" of radicals formed by the excited recoil atom.³⁻⁶ The present experiments show that a racemization process is occurring in this system, but that it has not been completed prior to the combination reaction in the liquid phase at 25°. We interpret the observation of competitive racemization and combination reactions as strong support for the importance of "cage" effects in keeping the reacting species in close proximity.

The experiments carried out at lower temperatures show that both temperature and phase effects can be observed, leading to increased racemization of the radioactive product, but with no appreciable effect on the *sum* of the yield of the two diastereomers. The results in the liquid phase are consistent with a slightly higher activation energy for combination (probably for diffusion together) than for racemization. The chloro-*sec*-butyl radicals presumably involved here are similar to those which exhibit "bridged-radical" behavior in photobromination,¹³ and such structures may possibly be involved during the racemization process. Bridged radicals are, however, not required on the basis of the present data alone. The low temperature results demonstrate also that the physicochemical differences between diastereomers also affect the degree of racemization observed for the radioactive products.

Since the nuclear histories of (n, γ) reactions can be quite different, comparison of these results with similar experiments for other (n, γ) halogen radioactivities, as well as with radioactive halogens from particle-emitting nuclear reactions, should be quite helpful in understanding the mechanism(s) involved in eq. 1.

(13) P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Am. Chem. Soc.*, **85**, 2849 (1963).

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Tritium Nuclear Magnetic Resonance Spectroscopy. I. Observation of High-Resolution Signals from the Methyl and Methylene Groups of Ethylbenzene. The Nonradiochemical Use of Tritium as a Tracer

Sir:

While proton n.m.r. spectroscopy has become commonplace, and deuterium n.m.r. spectra have been studied carefully¹ despite inherently low intensity and inferior resolution, to our knowledge high-resolution tritium n.m.r. spectroscopy is here reported for the first time. Our sample of neat ethylbenzene contained over-all 32.1 curies per ml. by conventional radioassay, which corresponds to about 1 atom % tritium. It was

(1) P. Diehl, and Th. Leppert, *Helv. Chim. Acta*, **47**, 545 (1964).

prepared by catalytic addition at room temperature of a small, measured amount of pure tritium, over palladium on charcoal, to the triple bond of phenylacetylene, followed by a large excess of hydrogen to achieve complete saturation of the side chain. The product was purified by bulb-to-bulb distillation and 0.3 ml. of it was transferred to and sealed in a high-quality n.m.r. sample tube.² By proton n.m.r. spectroscopy the chemical purity of the sample was confirmed, but owing to the low isotope content it was not possible to observe proton splitting by the tritium.

For observation of tritium our 40,000 Mc.p.s. Varian n.m.r. spectrometer was operated at *ca.* 8800 gauss. The sample temperature was 24°. The signal was weak but readily located by manual sweep from the proton region, and was self-identifying as it cannot be produced by any other material.³ High resolution was retained despite the large change in magnetic field, and some further improvement was achieved by means of the field-trimming coils. The spectrum consisted of two first-order multiplets, the higher-field one due to the $-\text{CH}_2\text{T}$ group being apparently a triplet of triplets. The splittings were analyzed by computer techniques to yield the coupling constants, $J_{\text{TCH}} = 13.8 \pm 0.1$ c.p.s. and $J_{\text{TCC}} = 8.11 \pm 0.06$ c.p.s. As a result of the low signal-to-noise ratio, it was not possible to detect the potentially greater complexity of the X part of an $\text{A}_2\text{B}_2\text{X}$ spectrum.⁴ The weaker peak, due to the $-\text{CHT}-$ group, was less clearly seen but appeared to be a doublet of quadruplets, as would be expected for X in an A_3BX case. The coupling constants were estimated from the computer analysis as: $J_{\text{TCH}} = 15.0 \pm 0.1$ c.p.s. and $J_{\text{TCC}} = 7.9 \pm 0.1$ c.p.s. If due allowance be made for the 6.66% higher magnetic moment of tritium,^{5b} one would predict J_{TCC} to be 8.10 ± 0.01 c.p.s. on the basis of the proton spectrum.^{5b} The observed chemical shift between the tritium peaks was 1.355 ± 0.006 p.p.m., in good agreement with (though 1% smaller than) the measured proton shift.^{5b} No signal was found for aryl tritium; it is estimated that no more than 5% of the tritium content could have been present in the ring.

Rather surprisingly, area measurements, made by planimeter upon well-displayed spectra run at a variety of power levels and swept in both directions, yielded the value 1.96 ± 0.06 for the $(-\text{CH}_2\text{T})/(-\text{CHT}-)$ ratio. If simple addition of T_2 prevailed, the ratio would be 1.00, while if catalytic randomization of the ethyl group occurred, the value would be 1.50. The ratio would indeed be 2.00 if randomization were complete at the tritiated styrene stage; additional experiments would of course be required to establish that point. By "randomization" is meant intra- and intermolecular

(2) Size E, available from Nuclear Magnetic Resonance Specialties, Inc., New Kensington, Pa. These inexpensive precision tubes, designed for use with the Varian A-60 spectrometer, were chosen for safety reasons, as they have slightly thicker walls than the Varian tubes. To clarify and strengthen them, S. L. Manatt has suggested briefly etching the outer surface with aqueous HF.

(3) Tritium has spin $1/2$, and its n.m.r. resonance frequency is the highest known for any nucleus, namely 45,414 Mc.p.s. at 10,000 gauss: (a) H. L. Anderson and A. Novick, *Phys. Rev.*, **71**, 372 (1947); (b) F. Bloch, A. C. Graves, M. Packard, and R. W. Spence, *ibid.*, **71**, 551 (1947).

(4) R. E. Richards and T. Schaefer, *Proc. Roy. Soc. (London)*, **A246**, 429 (1958).

(5) (a) R. E. Glick and A. A. Bothner-By, *J. Chem. Phys.*, **25**, 362 (1956), give 7.37 ± 0.10 c.p.s. (b) Our own measurements, based on an A_2B_2 analysis of the 60 Mc.p.s. spectrum of neat ethylbenzene, are $J_{\text{TCC}} = 7.59 \pm 0.01$ c.p.s. and $\delta = 1.369 \pm 0.002$ p.p.m., at 25°. Our error values are in every case stated as the standard deviation of the averaged value.