

of these mixtures of olefins resulted in product formation under competition conditions and made possible the computation of relative rate constants for both steps of the sequence. The experimental results for a mixture of isobutylene and *trans*-2-butene are summarized in the postulated reaction scheme.







Product ϵ is the only one obtained by two pathways. A separation is possible with the assumption that both triplet cyclopropylidenes would give the same ratio of *cis* to *trans* addition products; product ϵ is obtained

$$\beta/(\gamma + \delta) = (\eta + \mu)/\epsilon_{(\text{via B})}$$

90.7% via A and 9.3% via B.

The competition data are summarized in Table I, showing reactivities for (1) additions to C_1 to form cyclopropylidenes and (2) additions to cyclopropylidenes to form spiropentanes.

Table I

Olefin	Relative rates of olefin additions to	
	$H:C:$ (1)	 (2)
	1	20
	5	8
	15	10
	30	6
	32	1

The most striking feature of these data is the low reactivity of 1,3-butadiene in the first step, addition to C_1 , and the high reactivity in the second step, addition to a cyclopropylidene. For example, in competition with *trans*-2-butene the major products (93%) are those of addition of 1 molecule of 1,3-butadiene and 1 of *trans*-2-butene. The homoadducts of either olefin are small, totaling only 7%.

An explanation of these results can be made as follows: $C_1(^3P)$ displays greater reactivity through its filled and unfilled orbitals than through the half-filled orbitals, and it reacts with conservation of spin

angular momentum to make a triplet cyclopropylidene; the triplet cyclopropylidene reacts preferentially with 1,3-butadiene and nonstereospecifically with *cis*- and *trans*-2-butenes.

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Chemical Activation by the Br^{82m} Isomeric Transition. The Half-Life of Br^{82m}

Sir:

Recent reports^{2,3} show that radiative neutron capture by Br^{81} (49.5% natural abundance) produces predominantly Br^{82m} rather than the Br^{82} ground state previously assumed, the thermal neutron capture cross sections being 3.0 and 0.3 barns, respectively.³ The Br^{82m} decays to Br^{82} (36 hr.) by isomeric transition through a highly converted ($\alpha_k = 268$)³ 46-kev. level of Br^{82} . The half-life of the isomer has been reported as 4.98 ± 0.12 min.² and as 6.20 ± 0.05 min.³

Br^{80} atoms born from the isomeric transition Br^{80m} (4.4 hr.) \rightarrow Br^{80} (18 min.) are activated chemically⁴ as a result of the high nuclear charge⁵ generated

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(2) O. U. Anders, paper presented before the Division of Nuclear Chemistry and Technology at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(3) J. F. Emery, paper presented before the Division of Nuclear Chemistry and Technology at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(4) See, for example: (a) E. Segre, R. S. Halford, and G. T. Seaborg, *Phys. Rev.*, **55**, 321 (1939); (b) D. DeVault and W. F. Libby, *ibid.*, **55**, 322 (1939); (c) J. E. Willard, *J. Am. Chem. Soc.*, **62**, 256, 3161 (1940); (d) J. F. Hornig and J. E. Willard, **75**, 461 (1953); (e) R. M. A. Hahne and J. E. Willard, *J. Phys. Chem.*, **68**, 2582 (1964).

(5) S. Wexler, *Phys. Rev.*, **93**, 182 (1954); *J. Chem. Phys.*, **36**, 1929 (1962); "Actions Chimiques et Biologiques des Radiations," Vol. II, M. Haissinsky, Ed., Masson et Cie, Paris, 1965, pp. 157-179.

by internal conversion and subsequent Auger electron emission. To determine whether similar chemical activation occurs in the decay of $\text{Br}^{82\text{m}}$ we have dissolved neutron-irradiated Br_2 in CCl_4 at short times after irradiation, allowed it to stand, and looked for Br^{82} activity in organic combination following extraction of the Br_2 . The decrease in the amount of this activity as a function of the time after irradiation at which the bromine was mixed with the CCl_4 has been used to determine the half-life of $\text{Br}^{82\text{m}}$, and the data have been used to estimate the fraction of the decay events which lead to organically bound Br^{82} (36 hr.).

Quartz ampoules containing 0.1 ml. of degassed bromine were irradiated for 2 min. at a flux of 1×10^{12} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ in the rabbit tube of the University of Wisconsin reactor. Each ampoule was crushed in 5 ml. of CCl_4 at a different known time following the irradiation. The solution was then kept in a closed tube in the dark for 2 hr. to allow decay of any $\text{Br}^{82\text{m}}$. A 100- μl . sample was then removed for measurement of the total activity following which the Br_2 was extracted from the remainder of the CCl_4 with aqueous Na_2SO_3 . After allowing 48 hr. for decay of $\text{Br}^{80\text{m}}$ the aqueous and organic layers were each counted in a well-type scintillation counter to determine the Br^{82} (36 hr.) activity. To correct for any differences in the amounts of bromine in different ampoules or in the neutron exposure which they received, the counting rates of the extracted CCl_4 layers were normalized to each other on the basis of the total Br^{82} activity in the unextracted sample. Control runs in which the irradiated ampoule of Br_2 was crushed under CCl_4 after all of the $\text{Br}^{82\text{m}}$ had decayed, and then analyzed after the usual time of standing, yielded an average of 0.9% of the Br^{82} (36 hr.) in the CCl_4 layer. This value was subtracted as a correction to the total Br^{82} found in the CCl_4 in each of the $\text{Br}^{82\text{m}}$ experiments.

The presence of substantial fractions of the Br^{82} activity in the CCl_4 layers confirmed the expectation of chemical activation by the isomeric transition. The specific counting rates of Br^{82} (36 hr.) in these fractions at a fixed time after the irradiation are plotted in Figure 1 as a function of time from the end of irradiation until the Br_2 ampoule was broken in the CCl_4 .

The amount of activity in each CCl_4 layer is proportional to the amount of $\text{Br}^{82\text{m}}$ in the Br_2 at the time of mixing. Therefore, the slope of the plot in Figure 1 allows a calculation of the half-life of the $\text{Br}^{82\text{m}}$. The value obtained is 6.2 ± 0.1 min., in good agreement with the value of 6.2 ± 0.05 reported by Emery.³ By back-extrapolation of the data of Figure 1 to the midpoint of the 2-min. irradiation time, the hypothetical counting rate of Br^{82} produced in the CCl_4 layer by Br_2 dissolved instantly after an instantaneous irradiation can be estimated. The ratio of this counting rate to the total Br^{82} rate extrapolated to this time, and corrected for the Br^{82} produced in the ground state by neutron capture (9% of the total), is the "organic yield" (fraction of isomeric transition events for which the Br^{82} daughter atoms are fixed in organic combination). The value obtained (39%) agrees within the experimental error with the organic yield of Br^{80} observed earlier^{4d} from the $\text{Br}^{80\text{m}} \rightarrow \text{Br}^{80}$ isomeric transition.

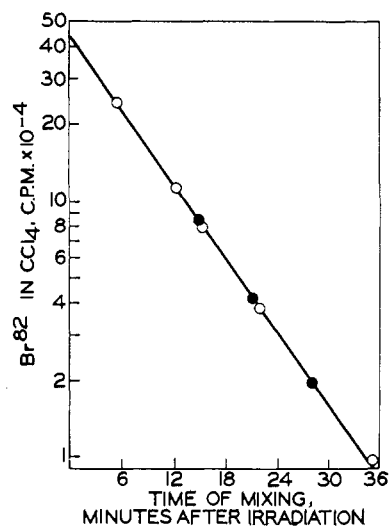


Figure 1. Br^{82} (36 hr.) in organic combination as a result of isomeric transition in $\text{Br}_2(\text{Br}^{82\text{m}})\text{-CCl}_4$ solutions; open and closed circles indicate separate series of experiments.

Although many investigations of chemical activation by radiative neutron capture by Br^{81} have been made, it is not wholly surprising that the existence of the $\text{Br}^{82\text{m}}$ isomer was not recognized earlier because most work with Br^{82} has involved long times of irradiation and standing relative to the 6-min. half-life, and because the presence of Br^{80} (18 min.) would tend to obscure the $\text{Br}^{82\text{m}}$ under the conditions of most of the experiments done. It must now be recognized that essentially all of the yields and product distributions which have been reported for chemical activation by radiative neutron capture by Br^{81} have been the result of isomeric transition following the (n,γ) process rather than of the (n,γ) process itself.⁶

The distribution of organic products resulting from the $\text{Br}^{82\text{m}}$ isomeric transition seems to be similar to that produced by the transition of $\text{Br}^{80\text{m}}$. This is indicated by comparison of the relative yields of some 20 Br^{82} -containing products from the neutron irradiation of $n\text{-C}_3\text{H}_7\text{Br}$ with the yields of the same products from the $\text{Br}^{80\text{m}}$ isomeric transition in similar systems.⁷ Analogous similarities in products are observed for the two processes in $\text{Br}_2\text{-CCl}_4$ solutions.^{4d} The organic yields of the two processes and of the $\text{Br}^{79}(n,\gamma)\text{Br}^{80\text{m}}$ and $\text{Br}^{79}(n,\gamma)\text{Br}^{80}$ processes appear to be equal in at least a number of cases.⁸ It has been suggested⁹ that such similarities would be expected if the γ -cascade by which the atoms activated by the (n,γ) process lose their excess nuclear energy nearly always goes through a low-lying highly converted level which results in a vacancy cascade of electron emission following loss of the primary recoil energy from γ -emission.

(6) Current experiments in our laboratory indicate that the organic yield of the $\text{Br}^{81}(n,\gamma)\text{Br}^{82\text{m}}$ process in solutions containing 1.7 mole % Br_2 in CCl_4 is similar to that found earlier^{4d} for the $\text{Br}^{79}(n,\gamma)\text{Br}^{80\text{m}}$ process, i.e., ca. 33%. In these experiments extraction was completed within 15 sec. from the start of irradiation, and the separated phases were allowed to stand before counting until the $\text{Br}^{80\text{m}}$ had decayed.

(7) J. B. Evans and J. E. Willard, *J. Am. Chem. Soc.*, **78**, 2908 (1956).

(8) J. C. W. Chien and J. E. Willard, *ibid.*, **79**, 4872 (1957).

(9) P. R. Geissler and J. E. Willard, *J. Phys. Chem.*, **67**, 1675 (1963).

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