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Carbon-14 Recoil in Azobenzene–Stilbene Solid Solutions[1a]

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Chemical effects of the nuclear transformation, $N^{14}(n,p)C^{14}$, in azobenzene–stilbene have been studied as a function of varying composition of the solid solution. It has been observed that the yields of azobenzene-C^{14} and stilbene-C^{14} show a linear dependence on the mole fraction of the corresponding parent compound. Non-statistical carbon-14 distribution as a result of re-entry processes was found from degradation studies.

Introduction

Ever since the discovery by Szilard and Chalmers,[2] in 1934, that chemical reactions can result from the consequences of nuclear processes, the attempted elucidation of the chemical consequences of radiative neutron capture reactions has been the object of much experimental effort. A mechanistic approach to hot atom chemistry has appeared comparatively recently. No generalization has yet appeared which provides a unifying rationale of all currently available data. Several models, for example physical impact,[3] epithermal reactions,[4] random bond fragmentation[5] and the displacement spike,[6,7] which emphasize physical considerations, have been suggested. Models stressing the importance of chemical environment have also appeared.[8–10]

The reactions of recoil carbon-14 are of considerable interest since they can be utilized in labeling organic compounds. The actions of the recoil fragment have been studied in this Laboratory both from the mechanistic and from the applied point of view. When the energy of the carbon-14 has been reduced to a level sufficiently low to permit bond formation, the particle will have traveled a considerable distance from its birthplace. The nature and state of the fragment at this moment is still a matter for speculation.

Tritium labeling of organic solids may be achieved through neutron irradiation of heterogeneous mixtures of the desired substances with inorganic lithium salts.[11] This method will not work well in the case of carbon-14 owing mainly to the shorter path length of the fragment.[9,12] External nitrogen sources can be utilized only in those cases where homogeneous mixing is achieved through solution or the formation of complexes. It was therefore of interest to study a homogeneous solid in which the chemical composition could be varied without appreciably changing the physical state of the material. The azobenzene–stilbene[13] system was chosen since the crystals of the constituents are isomorphous. They form near-ideal solid solutions,[14] are similar in structure and have similar radiation stability. This has allowed us to study the chemical effects of the nuclear transformation $N^{14}(n,p)C^{14}$ as a function of varying mole percentages of azobenzene in stilbene.

Experimental

Materials.—Azobenzene, stilbene, benzalaniline and phenylbenzylamine were Eastman Kodak Co. white label products. The first two compounds were further purified by vacuum sublimation before use. The palladium-on-charcoal catalyst was purchased from the Baker Chemical Co. All other reagents, solvents and carriers were reagent grade and used as received.

Sample Preparation.—The solid solutions of azobenzene and stilbene were made by fusing weighed amounts of the two components. A homogeneous melt of each composition was allowed to solidify and the solid solution subsequently ground into a fine powder. Quartz vessels designed to minimize air diffusion through the use of long capillary tubing[15] were utilized as containers. Samples with very low azobenzene content, however, were carefully degassed under high vacuum and irradiated in sealed quartz tubes.

Neutron Irradiation.—All irradiations were carried out in the center of the Brookhaven nuclear reactor for periods ranging from 5 to 12 days. The water-cooled hole operating at an ambient air temperature of about 30° was used for all samples except those which were sufficiently high melting so that they could be irradiated in air-cooled facilities operating at 50 and 80°. The thermal neutron flux in each reactor facility was monitored occasionally by activation studies on manganese. Two small pieces of aluminum foil containing 0.08% manganese (one of which was shielded from slow neutrons by cadmium) were subjected to pile neutron irradiation for 10 minutes. Neutron fluxes were calculated from the known capture cross section and the resultant manganese activity. The thermal neutron flux was taken as the difference between the total neutron flux and the fast neutron flux.

Radioassay.—The total carbon-14 activity produced in each irradiated sample was obtained by analysis of a small portion of the mixture by the method of Christman, Day, Hansell and Anderson.[16] The value thus obtained was generally higher than that calculated from the assumed thermal neutron flux. The various products were assayed

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

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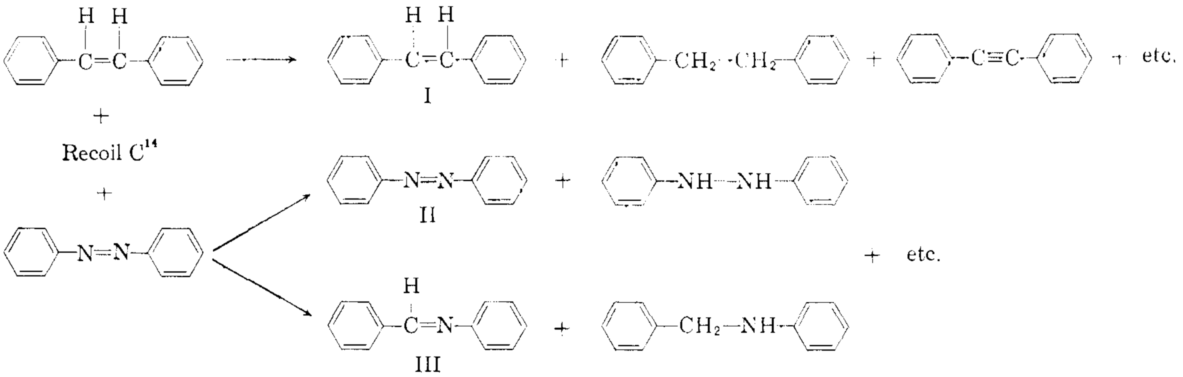

Fig. 1.—Re-entry products from azobenzene and stilbene.

by the same method after having been brought to chemical and radiochemical purity.

Gas-Liquid Chromatography.—Gas-liquid partition chromatography was employed for the final purification of the desired products. Eight-ft. columns, 0.5 inch i.d., packed with 60–80 mesh fire brick coated with Dow-Corning silicone oil 710 were used. Benzene and toluene were purified by employing a packing with 35% by weight of silicone oil as the stationary phase. The column was operated at 90° and the helium carrier gas flow rate was about 150 ml./min. The purification of methyl benzoate was carried out at 180° on columns packed with fire brick coated with 20% by weight of silicone oil as the stationary phase. The effluent gas flow rate was 200 ml./min.

Sample Processing.—Sublimation of the irradiated mixtures was carried out *in vacuo* in order to remove the polymeric substances produced. Desired compounds were first added to the sublimation vessel in weighed amounts. These carriers were heated together with the irradiated material to just above the melting temperature of the mixture and then held there until uniform mixing could be achieved. After cooling to room temperature, vacuum was applied to remove volatile substances from the mixture. The sublimate mixture thus obtained was then subjected to reduction by hydrogen transfer from cyclohexene in ethanolic solution with 10% Pd-on-charcoal as the catalyst.[17] Azobenzene was thus hydrogenolyzed to aniline, stilbene was converted to bibenzyl, and benzalaniline as well as phenylbenzylamine were debenzylated to give toluene and aniline.

Benzalaniline-C^{14}.—Benzalaniline-C^{14} was converted to its debenzylation product toluene-C^{14}, through catalytic hydrogen transfer. The reaction mixture following catalytic hydrogen transfer was neutralized with 2% aqueous HCl. The volatile components were removed by distillation. Toluene-C^{14} was partially recovered from the distillate by means of careful fractionation through a 38 cm., 12 mm. i.d., glass helix-packed column. It was then brought to radiochemical purity by employing gas-liquid chromatography.

Stilbene-C^{14}.—Stilbene-C^{14} was converted to bibenzyl-C^{14}. The bibenzyl-C^{14} was oxidized with permanganate to benzoic acid. Benzoic acid was converted to methyl benzoate and the latter brought to radiochemical purity.

To the residue resulting from the removal of volatile components from the hydrogen transfer reaction mixture an additional amount of 2% aqueous HCl was added. From this mixture, bibenzyl was isolated by petroleum ether (b.p. 30–60) extraction. The solvent was dried over calcium chloride and subsequently evaporated. The crude bibenzyl was subjected to alkaline permanganate oxidation.[18] The resulting benzoic acid was recrystallized and then converted to methyl benzoate through acid-catalyzed esterification with methanol. The methyl ester was brought to radiochemical purity by triple distillation through a Vigreux column. Further purification by means of gas-liquid chromatography did not result in any change in specific activity of this compound. Final proof of radiochemical purity was provided by hydrolysis of the ester and radioanalysis of the resultant benzoic acid The specific activity of this pure material was used to calculate the radiochemical yield of stilbene.

Azobenzene-C^{14}.—Aniline-C^{14} was isolated from the catalytic hydrogen transfer reaction mixture as its hydrochloride.

The aqueous aniline hydrochloride solution remaining following removal of non-polar substances from the reaction mixture was neutralized with 20% aqueous NaOH. The suspension obtained was extracted with ether. The ethereal solution was dried over sodium hydroxide pellets for several hours. Passing anhydrous hydrogen chloride through the dried solution readily yielded a precipitate of aniline hydrochloride. Reductive deamination[19] of the latter with hypophosphorous acid as the reducing agent gave benzene as the product. Radiochemical purification of the benzene was readily carried out by gas-liquid chromatography, toluene being added as a carrier to facilitate the removal of radioactive contaminants. The radiochemical yield of azobenzene is directly relatable to the activity of this benzene.

Degradations.—Toluene-C^{14} from benzalaniline was converted to benzoic acid by alkaline permanganate oxidation.[18] Methyl benzoate-C^{14} from stilbene was hydrolyzed in base. Benzoic acid was obtained from the neutralized reaction mixture. Benzoic acid from either source was recrystallized from hot water and then subjected to Schmidt decarboxylation by the method of Phares as modified by Anderson and Wolf.[20] Radiochemical balance was checked by summing the specific activities of the degradation fragments, *i.e.*, carbon dioxide and aniline (isolated as acetanilide). For the most part, however, the percentage activity in the carbon atoms of the aromatic nucleus was calculated by difference.

Results

In Szilard–Chalmers processes involving recoil carbon fragments, a complex mixture of products generally results. For the purposes of experimental expediency, we have chosen to study only the radiochemical yields of the various reentry[15] products as a function of varying composition of azobenzene–stilbene solid solutions. Since the effects of the chemical environment on the operations of a recoil carbon giving rise to a re-entry product depend mainly on the fragmentation and recombination of carbon–carbon bonds, no effort was made to differentiate between the products differing only in their degree of unsaturation. Probable re-entry products arising from carbon-14 recoil in the azobenzene–stilbene system are illustrated in Fig. 1.

For ease of chemical separation of the desired products and simplification of the experimental procedure, catalytic hydrogen transfer with cyclo-

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TABLE I

CARBON-14 REENTRY IN AZOBENZENE–STILBENE SOLID SOLUTIONS

Mole % azobenzene in target	Total C^{14} produced, μc.	Radioassay of carbon-14 activities, μc.					
		Azobenzene[a]	Stilbene[b]	Ring carbons[c] in stilbene	Exocyclic[d] carbons in stilbene	Benzal-[e] aniline	Exocyclic[f] carbons in benzalaniline
2.33	6.40	0.009	0.227	...	...	...	...
10.26	9.53	.038	.300	...	0.075	...	...
10.26	9.32	.037	.293	...	...	...	...
10.03	9.15	...	.304	...	...	0.014	...
20.56	23.3	0.160	.676	...	0.160	...	...
20.56	23.0	.162	.663	...	...	...	...
28.80	15.5	.120	.393	0.297	0.098	...	...
49.31	56.0	.685	1.07	...	...	...	...
49.31	43.7	.568	0.869	0.658	0.217	...	...
71.55	50.5	.869	.644	0.459	0.184	0.166	0.140
71.55	55.7	.973	.776	...	...	0.148	0.129
100	46.6	1.12	...	...	...	...	...
100	59.5	1.46	0.058	...	...	...	...

[a] Assayed as purified benzene. [b] Assayed as purified methyl benzoate. [c] Assayed as acetanilide from benozic acid degradation residue. [d] Assayed as CO_2 from Schmidt decarboxylation of benzoic acid. [e] Assayed as purified toluene. [f] Assayed as CO_2 from benzoic acid degradation.

hexane as the hydrogen source was carried out. Azobenzene-C^{14} (II) was thus converted to aniline-C^{14}. Benzalaniline-C^{14} (III) was converted to toluene-C^{14}. Stilbene-C^{14} (I) was obtained in the form of bibenzyl. To facilitate radiochemical purification, aniline-C^{14} was converted to benzene-C^{14}. Bibenzyl-C^{14} was oxidized to benzoic acid-C^{14}. The benzoic acid was esterified to give methyl benzoate. Results from radioanalyses of these compounds and their degradation products are given in Table I. The radiochemical yield expressed as percentage total activity in azobenzene-C^{14}, stilbene-C^{14} and in the ring carbons of stilbene-C^{14} can be seen plotted against the mole fraction of azobenzene in the solid solution in Fig. 2.

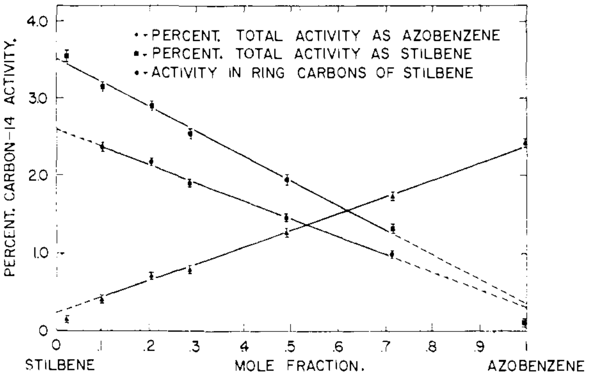


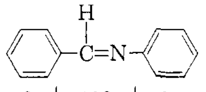
Fig. 2.—Radiochemical yields of re-entry products from azobenzene–stilbene.

As shown in Fig. 2, the yield of each re-entry product arising from carbon replacement is essentially a linear function of the mole concentration of the corresponding parent with some possible deviation at the extreme ranges of the solid solution system. The yield of azobenzene-C^{14} does not extrapolate to zero at 0% azobenzene, and its yield at a very low concentration of the parent appears to drop below the linear extrapolation. A small but non-negligible yield of stilbene-C^{14}, probably arising from fragmentation processes, is found when azobenzene is irradiated neat.

The replacement of aromatic ring carbons in stilbene as compared to the ring carbons in azobenzene appears to be essentially statistical. The ratio of radiochemical yield of benzalaniline-C^{14} to azobenzene-C^{14}, which is a reflection of the ease of nitrogen replacement to ring carbon replacement, is also roughly statistical. On the other hand, the carbon-14 distribution in stilbene was not random. The replacement of an ethylenic carbon takes place about twice as readily as the replacement of a ring carbon.

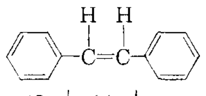
Degradation of the toluene-C^{14} from benzalaniline showed that 86% of the carbon-14 activity was present in the methyl group. Similar studies on the benzoic acid-C^{14} from stilbene showed that 26% of the activity was in the two ethylenic carbons. The theoretical values for random or specific distribution where these apply are compared to the found values in Fig. 3.

BENZALANILINE-C^{14} FROM AZOBENZENE



Theor.	0	100	0
Found	14	86	Not detd.

STILBENE-C^{14} FROM STILBENE



Theor.	43	14	43
Found	37	26	37

Fig. 3.—Carbon-14 distribution in re-entry products.

Discussion

Miller, Gryder and Dodson found the yield of radioactive carbon tetrachloride in mixtures of silicon tetrachloride–carbon tetrachloride to be very nearly proportional to the mole fraction of carbon tetrachloride in the irradiated solution. They pointed out that this behavior is consistent with the predictions of the billiard ball collision theory; nevertheless one need not invoke this theory in order to rationalize the similar behavior we have observed for the azobenzene–stilbene system. We need only assume that the probability for collapse to a stable entity (*cf.* ref. 15) once the molecule has been entered (to give re-entry product) is roughly the same for each component of our system. This is strikingly demonstrated by comparing the activities to be found in the benzene rings of the two components in our system (Fig. 2). It can be seen that the line which has been corrected for the exocyclic carbon activity in stilbene crosses the azobenzene curve very close to 0.5 mole fraction and that the ring activity yield of stilbene and azobenzene are nearly equal when comparing pure azobenzene to an extrapolated value for stilbene (*i.e.*, 0.0 mole fraction azobenzene). Ring entry is apparently not affected by the nature of the exocyclic structure. The nature of this particular replacement act must be such that multiple bond rupture does not take place in the molecule. If such rupture took place it would seem reasonable to expect considerable difference in yield between azobenzene and stilbene since the molecular debris produced from each of these molecules would certainly be quite different in chemical reactivity. Such statistical behavior is only possible when the character of the excited states of each species leading to product is similar.[15]

An example of non-statistical behavior[15,21] is also to be found in this study by considering the carbon-14 distribution in stilbene-C^{14}. Replacement of ethylenic carbons takes place twice as readily as ring carbons. This is to be contrasted with replacement of carbons in toluene to give toluene-C^{14} where replacement of ring carbons is favored. These facts serve to emphasize the restricted validity of statistical considerations and again underline the importance of the nature of the chemical environment.

The observed formation of stilbene-C^{14} when a sample of pure azobenzene was irradiated is probably due to fragmentation processes. The fact that neither line extrapolates to zero may be due to the yield from fragmentation processes (which processes seem to play a minor role) being added to the yield from the replacement process. This would demand that the extrapolated azobenzene yield at 0% azobenzene truly fall to 0 but that the yield of stilbene at 0% stilbene need not fall to 0. The azobenzene yield does indeed seem to fall off as expected. This fall off may in addition be due to the nature of the environment of the recoil fragment near the end of its track. At low azobenzene concentrations the crystal need no longer behave anisotropically with regard to the fragment path. The fragment may find itself preferentially directed to sites with low azobenzene content; consequently, re-entry in stilbene is favored. This, of course, may also beg the question as to whether or not the mixture is a true solid solution in this concentration range.

The carbon-14 distribution in toluene-C^{14} resulting from the hydrogenolysis of benzaniline (from nitrogen replacement in azobenzene) is the same as that found in toluene-C^{14} arising from the replacement either of hydrogen in benzene or of nitrogen in aniline.[9,21] Further, the percentage of gross activity found in these products is roughly the same in each case (statistical factors such as 6 equivalent sites in benzene having been adjusted for). This is consistent with the assumption that the same process may be involved in each case and again serves to underline the unimportance of the mass factor. (Clearly, the energetics of collisional deactivation by hydrogen are different from those involved in deactivation by nitrogen and carbon.)

No clear exposition of the nature of the reactive fragment or species based on the knowledge at hand is yet possible. One can speak of carbene (CH_2:) insertion reactions taking place because of the high energies involved. Statistical behavior in hydrogen replacement in other systems is certainly formally analogous to the reactions of a carbene. Without a knowledge of the statistical behavior of highly energetic methyl radicals or indeed of species such as non-solvated [CH_3^+], [$\dot{C}H$:], neutral atomic carbon, etc., the analogy lacks the force of convincing consistency. In the reactions involved in the system described in this paper, a displacement on carbon must be involved but one which has no formal analogy in presently understood systems. The difficulty lies in rationalizing the multiple bond rupture which must occur at the reactive site without concordant complete molecular disruption. A multicenter intermediate seems likely. Systems in which such a hypothesis can be tested are under study.

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