$$\frac{k_2'\,(\mathrm{H})}{k_7\,(\mathrm{R})} \sim \frac{(6 \times 10^{-14})(9 \times 10^{6})}{(1.2 \times 10^{-19})(7 \times 10^{10})} \sim 6 \times 10^{1}$$

$$\frac{k_2'\,(\mathrm{C_2H_4})}{k_8\,(\mathrm{RH})} \sim \frac{(6 \times 10^{-14})(3.2 \times 10^{17})}{(6 \times 10^{-17})(2.3 \times 10^{19})} \sim 14\ (?)$$

$$\frac{(k_3 + k_4)\,(\mathrm{R})}{k_7\,(\mathrm{olefin})} \sim \frac{(1.2 \times 10^{-10})(7 \times 10^{10})}{(1.2 \times 10^{-19})(3.2 \times 10^{17})} \sim 2 \times 10^{2}$$

$$\frac{(k_3 + k_4)(\mathrm{R})}{k_5\,(\mathrm{RH})} \sim \frac{(1.2 \times 10^{-10})(7 \times 10^{10})}{(4 \times 10^{-21})(2.3 \times 10^{19})} \sim 1 \times 10^{2}$$

These estimates are all very approximate since the actual rate constants will vary with the radical identity. However, they indicate that the only doubtful approximation is that H atom abstraction is negligible compared to addition to olefin at low olefin concentrations.

B. Neutralization Reactions.—The recombination coefficients for reactions 19 and 20 are

$$\mathrm{A^+} + {}^- \longrightarrow \mathrm{A^*} \qquad (19)$$

$$\mathrm{A^+} + \mathrm{B^-} \longrightarrow \mathrm{A} + \mathrm{B}\ \text{or}\ \mathrm{A{-}B^*} \qquad (20)$$

estimated to be 10^{-8} cm.^{3}/molecule-sec. and 10^{-6} cm.^{3}/molecule sec., respectively.[23] The much more rapid ion recombination keeps the steady-state ion concentrations to much lower values than radical concentrations, and makes ion–radical interactions very unlikely.

C. Rate Constants at 25°

Reference	Reaction	Rate constant cm.^{3}/molecule sec.
(10), (9)	$\mathrm{H} + \mathrm{C_2H_4} \longrightarrow \mathrm{C_2H_5\cdot}$	$k_2 = 6 \times 10^{-14}$
(10), (9)	$\mathrm{H} + \mathrm{CH_3CH{=}CH_2} \longrightarrow \mathrm{CH_3\dot{C}HCH_3}$	$k_6 = 9 \times 10^{-14}$
(27), (14)	$\mathrm{H} + \mathit{Cyclo}\text{-}\mathrm{C_3H_6} \longrightarrow$ $\mathrm{H_2} + \mathrm{C_3H_5}$	(?) $k_8 = 6 \times 10^{-18}$ for $\mathrm{CH_4}$ $k_8 = 6 \times 10^{-17}$ for $\mathrm{C_2H_6}$
(25)	$\mathrm{CH_3^+} + \text{cyclo-}\mathrm{C_3H_6} \longrightarrow \mathrm{CH_4} + \mathrm{C_3H_5}$	$k_5 = 4 \times 10^{21}$
(26)	$\mathrm{CH_3} + \mathrm{C_2H_4} \longrightarrow n\text{-}\mathrm{C_3H_7\cdot}$	$k_7 = 1.2 \times 10^{-19}$
(24)	$\mathrm{CH_3\cdot} + \mathrm{C_2H_5\cdot} \longrightarrow \mathrm{C_3H_8}$	$(k_3 + k_4) \geq k_4 = 1.2 \times 10^{-10}$ $R_i \neq R_j$
(24)	$\mathrm{C_2H_5\cdot} + \mathrm{C_2H_5\cdot} \longrightarrow$	$(k_3 + k_4) \geq k_4 \cong 5 \times 10^{-11}$ $R_i = R_j$

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[23] G. Francis, "Ionization Phenomena in Gases," Academic Press, Inc., New York, N. Y., 1960.

[24] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1960, p. 302.

[25] A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951), as quoted in reference 24, p. 296.

[26] R. K. Brinton, *ibid.*, **29**, 781 (1958).

[27] Reference 24, p. 292.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

The Mechanism of Recoil Tritium Reactions with Hydrocarbons in the Liquid Phase[1]

BY EDWARD K. C. LEE AND F. S. ROWLAND

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The distribution of recoil tritium atoms among various molecular species after reaction with *trans*-hexene-2 or *trans*-butene-2 is quite similar for reactions carried out in gas and liquid phases. The principal differences are observed for those olefinic products (propylene, butene-1, pentene-1) which are formed primarily through decomposition of an excited free radical. The liquid phase yields for these are lower by factors of 2.5 to 8, consistent with more rapid collisional deëxcitation of the excited radical. The energetic reactions of the tritium atom itself are essentially the same in both the gaseous and liquid phases.

Introduction

Recoil tritium atoms are formed with kinetic energies in excess of 10^5 electron volts from either of the nuclear reactions, $\mathrm{Li^6(n,\alpha)T}$ or $\mathrm{He^3(n,p)T}$. Those atoms recoiling through the gas phase usually form a final, stable chemical bond in a chemical interaction which begins with the tritium atom still well above thermal kinetic energies. These gaseous reactions have been rather thoroughly studied,[2-4] especially with hydrocarbons, and the observed distribution of radioactive molecules has been explained satisfactorily. Recoil tritium reactions carried out in liquid or solid phases have shown that the reactions are qualitatively similar[2,5-7] to those occurring in the gas phase, but direct comparisons have not been previously performed.

We have investigated the distribution of tritium radioactivity among various molecular products for *trans*-butene-2 and *trans*-hexene-2 in both the gaseous and liquid phases to determine the similarities and differences arising in recoil tritium reactions that can be attributed to the phase in which the reactions occur. The postulated gas phase mechanisms for each olefin include reactions which should be sensitive to the concentration changes between gas and liquid.

Experimental

Chemicals.—The *trans*-hexene-2 was an A.P.I. Standard sample containing 0.08 ± 0.02 mole per cent. impurities. *trans*-Butene-2 was obtained from Matheson Company in lecture bottles and usually contained *n*-butane and butene-1 as the chief impurities, both approximately 0.1%. $\mathrm{He^3}$ was purified from tritiated impurities as usual.[3]

Irradiated Samples.—For liquid phase irradiation, the hydrocarbons have been sealed with powdered LiF in glass

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[1] Research supported by A.E.C. Contract No. AT-(11-1)-407.

[2] F. S. Rowland, J. K. Lee, B. Musgrave and R. M. White, Proceedings of the Symposium on the Chemical Effects of Nuclear Transformations, I.A.E.A., Prague, Czechoslovakia, October, 1960.

[3] J. K. Lee, B. Musgrave and F. S. Rowland, *J. Am. Chem. Soc.*, **82**, 3545 (1960).

[4] R. Wolfgang, *et al.*, Proceedings of the Symposium on the Chemical Effects of Nuclear Transformations, I.A.E.A., Prague, Czechoslovakia, October, 1960; D. Urch and R. Wolfgang, *ibid.*, **83**, 2982 (1961).

[5] W. J. Hoff, Jr., and F. S. Rowland, *ibid.*, **79**, 4867 (1957).

[6] A. M. Elatrash, R. H. Johnsen and R. Wolfgang, *J. Phys. Chem.*, **64**, 785 (1960).

[7] M. Henchman and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2991 (1961); J. G. Kay, R. P. Malsan and F. S. Rowland, *ibid.*, **81**, 5050 (1959).

capillaries made from 1720 Pyrex. The capillaries were loosely filled with LiF and evacuated. The hydrocarbon liquids were then condensed into the capillary at −196° until they had nearly filled it, and the capillary was sealed off. A small evacuated space was left during sealing to minimize pyrolysis of hydrocarbon by contact with the hot glass. The irradiation geometry was very irregular, but the amount of gas occupying this space during irradiation was very small, and the contribution of recoil tritium reactions with gaseous molecules is estimated as much less than 1%.

Each capillary was contained in a sealed, loose, polyethylene sleeve for protection and irradiated at ambient reactor temperature (about 20°). All of the capillaries were opened *in vacuo* by bending them to breaking in a ball-joint system, maintaining a tight external seal throughout.

The gas phase samples were prepared in the manner described previously.[3]

Gas Chromatographic Separation and Tritium Assay.—The procedure for gas chromatographic separation and gas proportional counting of aliquots of the irradiated samples has been fully described elsewhere.[3,8]

In our experience, handling of samples of higher boiling compounds can readily lead to fractionation in the taking of aliquots. This fractionation generally occurs through liquefaction of some of the parent hydrocarbon and/or through dissolution of some of the higher boiling radioactive products in either the stopcock grease or the liquefied parent. These errors can be minimized by handling the entire sampling process at an elevated temperature, but the total manipulation of a capillary sample at higher temperatures is an awkward process. Instead, we have handled the samples rapidly to avoid loss into stopcock grease and have introduced the aliquots into sample loops large enough to contain the entire parent as a gas. A typical aliquot of *trans*-hexene-2 will involve an 85 cc. sample at ~1.0 cm. pressure (~5 mg.).

These large, low pressure loops have not given difficulty when the flowing helium stream (at 2.3 atmospheres) was switched from the by-pass through the sample loop. The parent mass and radioactivity peaks are not unduly spread as shown in Fig. 1. The shape is approximately the same as that exhibited by low boiling parent compounds, when they are present in amounts sufficient to overload the chromatographic column. Although the gas proportional counter is operated at room temperature, no background count rate difficulties have been observed such as might occur through condensation of radioactive products in the active volume of the counter.

The columns used for chromatographic analysis of hydrocarbons have been:

(a) 15-m. dimethylsulfolane (DMS), 30% by weight on firebrick, 24.0°, helium flow rate 25 ml./min., propane/helium ratio 1.44 in counter gas.

(b) 2.4-m. silica gel (80–150 mesh), 80°, helium flow rate 29 ml./min., C_3H_8/He ratio 1.31.

(c) 15-m. safrol, 30% by weight on firebrick, 0°, helium flow rate 45 ml./min., C_3H_8/He ratio 1.25.

The tritium-labeled iodides from an iodine-scavenged sample were analyzed on

(d) 3-m. orthotritolyl phosphate, 20% on firebrick, 97°, helium flow rate 45 ml./min., C_3H_8/He ratio 0.86.

The counting measurements were made with a gas proportional counter of either 20 ml. or 85 ml. active volume. The longer residence time of the radioactive gases in the latter (1.4 min. for DMS) improved the accuracy of measurement of the later peaks, while HT, CH_3T, C_2H_5T and C_2H_3T were resolved on the silica gel column. Aliquots were analyzed on the Safrol column for only a few samples.

Neutron Irradiations.—All but one of the irradiations were carried out in the turntable facility of the TRIGA reactor of the Veterans Administration Hospital in Omaha, Nebraska. The nominal neutron flux in these holes is 1.0×10^{11} n/cm.^{2}/sec. The actual neutron flux within the gas samples is somewhat reduced by neutron absorption in the Pyrex 1720 glass.

Number 138 was irradiated for one pulse in the corresponding location of the General Atomic Mark I Triga reactor in San Diego. This neutron pulse delivered the equivalent of a 30 minute Omaha irradiation in approximately 10 milliseconds. The peak neutron flux for this sample was about 6×10^{15} neutrons/cm.^{2}/sec.[9]

The longer range of the tritium recoils from $Li^6(n,\alpha)T$ causes an appreciable fraction of the total tritium to enter the capillary walls. Another important fraction of the tritium will reënter LiF crystals and be stopped there. Since the geometry is quite irregular, quantitative evaluation of the fraction of tritium in the hydrocarbon liquid and in the other locations has not been done.

Results

The distribution of tritium radioactivity among molecular hydrogen and the various hydrocarbon products is summarized in Table I for experiments with *trans*-hexene-2 as the parent hydrocarbon. Table II presents the results obtained from experiments with *trans*-butene-2. In all cases of comparisons, it is not apparent that there is any product of constant yield against which alterations can be readily measured. The *trans*-butene-2 yields in Table II have been set equal to 100, and all other activities expressed relative to it. The possibilities of error in measurement of *trans*-hexene-2 are much greater, so the gas phase propylene yield has been arbitrarily set as 22 and used as the base for relative values. The liquid phase runs have been normalized to the data of the first column by equating the total observed activities emerging in an 8-hour DMS run for each.

The identification of each radioactive species has been made by coincidence of the radioactivity with a calibration mass peak of the known compound. Since the DMS column has been calibrated for all of the likely C_4 and C_5 alkanes and alkenes and many of the unlikely hydrocarbons, this identification should be satisfactory for the lower boiling components. The activity peak appearing at 132 minutes on the DMS column has been identified as 1,3-butadiene.

The hexenes have not been calibrated with API standards, but with mixtures, and the identifications shown are not positive for *cis*- and *trans*-hexene-3. The peak prior to the parent in Fig. 1 is listed as *cis*-hexene-3 in Table I, while a small, uncertain amount of activity on the tail of the parent is designated as *trans*-hexene-3. Although the C_6 radioactivity peaks from irradiated *trans*-hexene-2 all coincide with mass peaks, overlap with smaller unidentified peaks cannot be ruled out since a large number of compounds which probably fall in this region (*e.g.*, C_4 and C_5 dienes, ene-ynes, etc.) have not been calibrated.

The tritium activity found in iodinated molecules from one iodine-scavenged sample is also indicated in Table II. The measurement on this aliquot is based relative to an early peak corresponding to all the HT and hydrocarbons appearing in the whole DMS run.

Mass peaks were recorded for each sample and always showed less than 1.5% non-parent hydrocarbons after irradiation, with the exception of No. 130, for which appreciable isomerization to *cis*-hexene-2 occurred. Some typical mass analyses are listed in Table III.

Most of the errors in the tables are calculated *only* for the standard deviation in the ratio arising from the random statistics of counting and are

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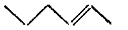
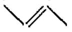
[8] F. S. Rowland, J. K. Lee and R. M. White, TID-7578, U.S.-A.E.C., p. 39 (1959); J. K. Lee, *et al.*, *Anal. Chem.* (in press).

[9] The flux *vs.* time characteristics of this neutron pulse are described in GA-1695 available from General Atomic, San Diego.

TABLE I

DISTRIBUTION OF RADIOACTIVITY FOLLOWING RECOIL TRITIUM REACTIONS WITH *trans*-HEXENE-2

Phase	Gas (cm.)[a]							Liquid (mg.)[a]	
Number	132	125	123	126	129	130	[b]	136	135
t-Hexene-2	12.3	9.3	6.2	4.4	10	11	~10	...	...
He^3	1.1	1.2	1.2	1.2	1.1	1.1	~ 1	...	...
LiF	...	...	...	...	...	...	...	5.0	5.0
Other	...	...	...	11.6 (O_2)	(I_2)	3.6(NO)	...	...	...
Total disint. DMS aliquot × 10^{-4}	20	22[d]	14	7	21	18[e]	...	10	2[c]
	104 ± 1	92	89	84	81	92	52	103 ± 1	100 ± 2
HT	187 ± 2	179	170	150	188	177	195	210 ± 2	
CH_3T	7.2 ± 1.0	7.2	6.0	6.5	5.8	5.0	8	11.2 ± 0.6	222 ± 4
	(22)	(22)	(22)	(22)	(22)	(22)	(22)	5.2 ± 0.2	5.2
	9.9 ± 0.2	9.0	10.0	9.0	8.6	8.9	10	4.2 ± .3	4.3
	14.1 ± .2	14.3	14.3	15.3	14.0	14.1	16	2.1 ± .1	2.2
	1.4 ± .1	1.1	1.5	0.9	1.3	1.0	2	2.0 ± .1	1.7
	1.9 ± .1	1.9	1.9	1.1	1.6	1.3	1	2.7 ± .1	3.7
	3.9 ± .5	4.1	5.2	1.7	2.2	2.2	4	5.2 ± .5	6.2
	2.9 ± .2	2.9	2.9	1.1	1.6	1.5	1	2.8 ± .1	2.9
=	6.8 ± .8	6.7	5.8	5.3	5.9	4.2	6	4.2 ± .5	3.2
132 min.	2.1 ± .2	2.3	3.2	3.1	1.7	0.9	...	<0.1	...
	6.1 ± .5	5.0	5.1	1.6	1.9	24.0	6	6.9 ± .5	8.2
	1.1 ± .5	0.7	0.5	0.4	1.2	1.9	6	1.1 ± .5	6.5
	7.4 ± .5	6.8	7.1	2.3	3.1	20.7	...	5.6 ± .5	
	4.3 ± .5	4.0	3.4	1.0	2.3	14.9	...	4.1 ± .5	2.9
	26.9 ± .5	20.6	19.0	<0.1	2.6	0.3	16	36.9 ± .5	37

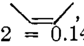
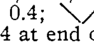
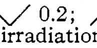
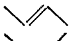
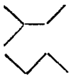
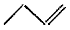
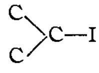
[a] All gas phase samples irradiated for 1 hr. at 1.0 × 10^{11} n./cm.^{2}/sec., both liquid phase samples irradiated for 2 hr. at 1.0 × 10^{11} n./cm.^{2}/sec. [b] Ref. 10; 6 days at 2 × 10^9 n./cm^2./sec. [c] 20 cc. counter. [d] Also , 1.0; ≡, 0.8;  0.3; , 0.4;  0.2;  0.4. [e] Appreciable macroscopic isomerization to *cis*-hexene-2 (*cis*/*trans* for hexene-2 = 0.14 at end of irradiation).

TABLE II

DISTRIBUTION OF RADIOACTIVITY FOLLOWING RECOIL TRITIUM REACTIONS WITH *trans*-BUTENE-2

Number	58	57	138	37	39	43	44	45	Gas phas 1 atmos. [d]
	trans-Butene-2 + LiF					*trans*-Butene-2 plus LiF and I_2			
Irradiation time (hr.)	3		[a]	3.5					
Total activity disint. × 10^{-3}	27[b]	17	14	26	22	13	31	18[c]	
	(105)	(100)	(100)	(105)	(105)	(105)	(105)	(105)	(105)
		5 ± 1	5						
	33	35 ± 1	23	29	11	10	13	33	31
	17	17 ± 1	16	17	20	17	16	20	61
	5	5 ± 1	7	8	6	6	8	7	5
	17	17 ± 1	18	16	14	17	17	18	14
HT	184	188 ± 4	178	191	191	196	177	199	189
CH_3T				12 ± 1	10	11	11		
—	1.7 ± 0.3								1
=	2.4 ± 0.3	4 ± 1	4	4	4	5	3	6	4

[a] Irradiated for approximate 10^{-2} sec. at 6 × 10^{15} n./cm.^{2}/sec. [b] Also , 1; ≡, 1; , 1; pentenes, 2. [c] Also CH_2TI, ~2; C–C–I,  $\underset{C}{\overset{C}{>}}C—I$, C–C–C–I, each ~1. [d] Ref. 3, 48 hr. at 2 × 10^9 n./cm.^{2}/sec.

listed for representative samples. However, the quantitative resolution of the hexene peaks is somewhat arbitrary and hence less precision is attached to them. The errors listed for CH_3T and C_2H_3T depend upon the separation with the silica gel column, and this aliquot was usually smaller with less activity in each peak, and hence lesser accuracy.

Examinations of similar samples such as the first three of Table I show that the largest discrepancies occur for HT, the parent and *n*-hexane. The inequality in *trans*-hexene-2 pressure among the three samples would contribute to these differences in ratios causing changes in the observed directions.[3]

Discussion

Similarity of Distributions in Liquid and Gas Phases.—The qualitative distribution of radioactivity is essentially the same for the *trans*-hexene-2 molecule in both gas and liquid phases.

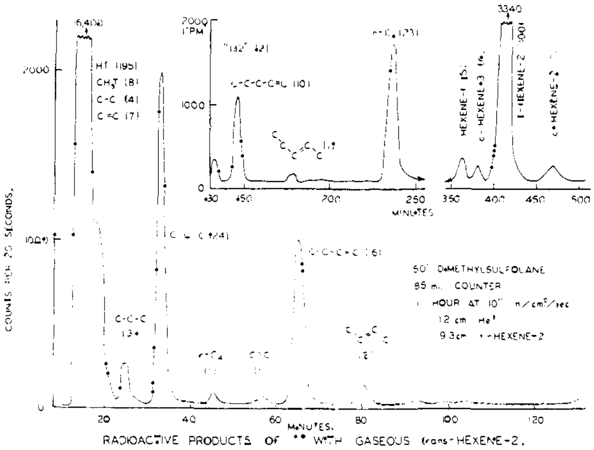
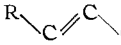
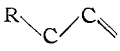
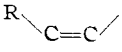


Fig. 1.—Radioactive products of T* with gaseous *trans*-hexene-2.

TABLE III

MASS ANALYSIS OF TYPICAL RECOIL TRITIUM SAMPLES AFTER IRRADIATION

Number	Relative peak areas 132	136	58	43
	100	100	100	100
	See hexenes	0.01	0.03	0.05
		.06	.32	.42
R-C-C-C	≤0.05	.03	.08	.41
CH_4	≤.01	.003	~0.05	
C-C	≤.01	..	.0004	.007
C=C	.02	~ .005	.004	.007
C-C-C	≤.01	..	.007	
C—C=C	.03	.005	.42	.44
Other hexenes	≤.10	.10	..	..

and the quantitative comparison of yields (*viz.*, No. 132 *vs.* No. 136) shows that most of these labeled products are formed in closely comparable amounts in each. All of the labeled molecules which arise chiefly from reactions 1 to 3 are phase-independent in yield to a good approximation

$$T^* + R—H \longrightarrow R—T + H\cdot \quad (1)$$

$$T^* + R—H \longrightarrow HT + R\cdot \quad (2)$$

$$T^* + R—R^1 \longrightarrow RT + R^1\cdot \text{ or } R\cdot + R^1T \quad (3)$$

These reactions have been postulated in the gas phase to arise from energetic reactions, occurring very rapidly, and which are controlled much more by the geometry of the encounter between the tritium atom and the target molecule than by the energetic requirements of various reactions.[2-4] The time of contact of the collision complex of the tritium atom plus molecule is assumed to be less than normal vibrational times. The conclusion immediately follows that these reactions occur so quickly and with so much energy available that the course of reaction is basically unaffected by the close proximity of other molecules. It has been pointed out previously that only a very small percentage of the total tritium activity is found in compounds requiring further reaction with neighboring molecules or radicals.[5,4]

The relative yields of HT, CH_3T, C_2's and butenes from *trans*-butene-2 are also practically unaffected by the phase change and again indicate the reactions leading to these products are insensitive to the phase of the target molecule.

Excited Free Radicals as Hot Products.—The radioactivity distribution observed for recoil tritium reactions with various olefins[4,10,11] and the pressure dependence of smaller olefin products[3] have both indicated that an important "hot" reaction leads to the formation of an energetic alkyl radical,

$$T^* + R—CH=CH—R^1 \longrightarrow R—\dot{C}H—CHT—R^{1*} \text{ or } R—CHT—\dot{C}H—R^{1*} \quad (4)$$

excited both by the kinetic energy of the tritium atom and by the exothermicity of the reaction. This excited radical can then react further by either decomposition or deëxcitation.

This competition is pressure dependent in the gas phase and should greatly favor deëxcitation in condensed phases. Those radioactive molecules whose yields are markedly reduced in the liquid phase for both parent molecules are just those resulting from the decomposition of the radicals from (4). Some of the pentene-1 and propylene formed in both phases may arise from the reactions analogous to (3) for direct replacement of the methyl or *n*-propyl radicals. However, since excited radical decomposition still persists in the liquid phase as shown by the non-zero yield of butene-1,[12] the radical decomposition mechanism is still probably the predominant formation mechanism for all three olefins from liquid *trans*-hexene-2.

Free radical scavengers (O_2, I_2, or NO) greatly reduce or eliminate the n-$C_6H_{13}T$ yield, as expected if the deëxcited radicals from (4) are precursors for all or most of the yield in unscavenged systems. Similarly, O_2 and I_2 depress the hexene yields as expected for molecules which are formed from disproportionation of thermal free radicals. It is difficult to distinguish the source of the hexene yield that is not removed by scavengers; decomposition of excited radicals by H atom loss, exchange reactions with parent, etc., may be partial contributors to the remaining yield of hexenes.

The effect of NO as a scavenger is complicated both by the isomerization of macroscopic amounts of the parent molecule and by failure of the scavenger to convert the radioactivity to relatively non-volatile products. The activity appearing as hexene-1 and *cis*-hexene-2 arises largely from decomposition of the original product formed by reaction of hexyl radicals with NO.[3]

Both C_2H_3T and the unidentified species (132 minute) also appear to involve excited precursors and are reduced or eliminated in the liquid phase.

Recombination Reactions of Tritium Atoms in Condensed Phases.—The yields of HT and CH_3T from *trans*-hexene-2 are slightly higher in the liquid phase than in the gas phase. Slight increases can arise readily from the much more favorable third-body conditions for recombination of thermalized

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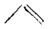
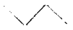
(10) D. Urch and R. Wolfgang, Proceedings of the Symposium on the Chemical Effects of Nuclear Transformations, I.A.E.A., Prague, Czechoslovakia, October, 1960.

(11) D. Urch and R. Wolfgang, *J. Am. Chem. Soc.*, **81**, 2025 (1959).

(12) Edward K. C. Lee and F. S. Rowland, *J. Chem. Phys.*, **36**, 55 (1962).

TABLE IV

SUMMARY OF RECOIL TRITIUM REACTIONS WITH METHANE AND ETHANE IN GAS AND LIQUID PHASE

	CH_4				C_2H_6			
	Gas			Liquid	Gas			Liquid
Additives	..	..	Br_2I_2 O_2	..	..	I_2	O_2	..
Products								
HT	62	50	29–35	39	43	56	52	42
CH_3T	20	32	32–36	49	4	4	3	5
C–C	3	8		6	28	31	28	38
C═C	..	..	<1	~0.3	..	3	3	~4
C≡C	..	..		..	..	0	Tr.	..
	..	..		..	..	0.4	0.4	..
	5	10		4	10	.5	Tr.	5
				2	10	.9	0	6
$>C_4$				~0.3	5	0	0	>0.3
MeI	..	..	..	..	..	4	..	..
EtI	..	..	..	..	..	0.9	..	..
Oxygen compounds	..	..	..	..	..	..	13	..
Neutron flux n./cm.²/ sec.	2×10^9	5×10^{12}	$\sim 10^{13}$	5×10^{12}	5×10^{12}	$2\sim 6 \times 10^9$	$2\sim 6 \times 10^9$	5×10^{12}
Approx. integral neutron dose 10^{15} n./cm.²	0.3	3–20	~2	0.1–0.2	3–20	0.3–4	0.3–4	0.1–0.2
References	(13)	(13)	(16)	(14)	(13)[a]	(20)	(20)	(14)

[a] Very similar distributions have been reported in refs. 15 and 17.

tritium atoms with H atoms or CH_3 radicals. The corresponding reactions would be quite unlikely in the gas phase and the probable fate of such thermalized atoms would be addition to the olefinic parent with the ultimate formation of *n*-alkane or other radical-radical reaction products. In any case, the fraction of recoil tritium atoms involved in such reactions is not more than a few per cent. of the total yield. Most of the HT is formed in the hot reaction 2.

Thermalized tritium atoms may also react by addition to the parent molecule and hence be indistinguishable from energetic addition and subsequent deëxcitation of the radical. The source of the scatter in *n*-butane yields of Table II has not yet been determined. A variable contribution by diffusion of tritium atoms from the heterogeneous LiF surfaces into the parent may be involved.

The differences in product yield between gas and liquid phases for tritium reactions with olefins may be summarized as:

(a) Direct replacement reactions are basically the same in both phases.

(b) Excited free radicals, formed by energetic tritium atom additions, usually decompose to olefinic compounds in the gas phase, but are more often deëxcited by collision in the liquid phase, than being found as the usual recombination or disproportionation products.

(c) Thermalized tritium atoms, which are normally scavenged by the parent compound in the gas phase, may be somewhat more likely to react to form HT or CH_3T in the liquid phase.

Corresponding decreases in yield for other thermal tritium species in the gas phase are not readily distinguished since their yield is affected in opposite directions by (b) and (c).

Radiation Flux.—The single experiment with the pulsed neutron source provides a comparison over a range of approximately 5×10^4 in radiation intensity. No significant differences appear in the data of Table II for that run.

Methane and Ethane.—The only hydrocarbons which have been measured previously in both the gaseous and liquid phases are methane and ethane.[13–17] The distributions of radioactivity in the two phases were qualitatively similar, but quantitatively different as shown in the data summarized in Table IV. Since the reaction leading to the parent molecule is a hot reaction, as shown by the lack of effect of scavengers in the gas phase, the yield would be expected to be the same in both phases by comparison with the present series of experiments. However, the data of Table IV were not collected under directly comparable experimental conditions, and the observed differences may arise from these variations in the experiments.

The liquid phase experiments were carried out at −160° with a high ratio of powder to alkane (>10) and were analyzed by fractional distillation of carriers.[18] Radiation chemistry experiments carried out with high surface areas show reduced H_2 yields,[19] and a similar surface effect on recoil tritium reactions has been suggested to explain variations in the activity distribution obtained with C_2H_6 in the presence of silica gel.[17]

The most important experimental variations other than phase in Table IV are probably the integral neutron dose and the temperature of irradiation. Although all of the gas phase results

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(13) M. El-Sayed, P. Estrup and R. Wolfgang, *J. Phys. Chem.*, **62**, 1356 (1958).

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(15) A. A. Gordus, M. C. Sauer, Jr., and J. E. Willard, *J. Am. Chem. Soc.*, **79**, 3284 (1957).

(16) P. Estrup and R. Wolfgang, *ibid.*, **82**, 2661, 2665 (1960).

(17) T. Tsetskhladze, *et al.*, as reported by E. L. Andronikashvili, I.A.E.A. Conference on Programming and Utilization of Nuclear Reactors, Vienna, October, 1961.

(18) The measurement of C_2H_5T yield is relatively uncertain in these liquid-phase experiments, since no C_2H_6 carrier was added and the data were estimated from variations in the specific activity of carrier C_2H_6.

(19) J. M. Caffrey, Jr., and A. O. Allen, *J. Phys. Chem.*, **62**, 33 (1958).

(20) D. Urch and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2982 (1961).

shown for methane and ethane are in the integral neutron dose region for which similar experiments with cyclopropane have shown appreciable radiation damage alterations ($>10^{13}$ n./cm.^{2}),[21] only small effects should be expected for the labeled parent molecules. Gaseous ethane experiments carried out for lower integral neutron doses have considerably more HT and less of C_3 and heavier compounds, but approximately the same amount of parent.[22] Hence, the differences in parent yield with phase in Table IV are probably not associated with these integral dose differences.

Similarly, searches for temperature effects in recoil tritium reactions have not shown large effects on the T for H substitution,[5,13] although more extensive experiments are desirable.

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[21] J. K. Lee, B. Musgrave and F. S. Rowland, *Canad. J. Chem.*, **38**, 1756 (1960).

[22] A. Beyerlein and F. S. Rowland, unpublished results.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DETROIT, DETROIT 21, MICHIGAN, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNSYLVANIA]

Effects of High Energy Radiations on α,β,γ,δ-Tetraphenylporphine. II. Formic Acid, Acetic Acid and Propionic Acid as Solvents

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The stability of porphyrins toward irradiations was studied. α,β,γ,δ-Tetraphenyl porphine was used as a model system. The compound was irradiated in formic acid, acetic acid and propionic acid with 118 kV., 10 ma. X-ray and Co^{60} gamma rays and the eventual changes were followed spectrophotometrically. In contrast to the behavior in sirupy phosphoric acid and sulfuric acid, no significant changes were noted on irradiation with low dosages up to approximately 5000 r. The higher dosages produce changes, which were interpreted as destruction of the porphine ring. A mechanism involving one and/or two electron oxidation followed by disproportionation is suggested. Hydroxyl and perhydroxyl radicals as well as hydrogen peroxide and peracids seem to be responsible for the oxidation.

Introduction

It was shown in a previous paper[1] that tetraphenylporphine in syrupy phosphoric acid or sulfuric acid upon interaction with beta-particles or X-radiation undergoes a one and/or two electron oxidation, depending upon the irradiation dose. Identical changes were found to be produced by ceric ions and Fenton reagent. It was suggested that hydroxyl and perhydroxyl radicals were responsible for the oxidations.

The purpose of this paper is to present some results on the action of radiation on tetraphenylporphine in the organic acids, especially formic acid, acetic acid and propionic acid. All three acids are relatively good solvents for tetraphenylporphine, and the resulting solutions have absorption spectra characteristic of the acid salts. The changes occurring upon irradiation can be followed spectrophotometrically, by observing the intensity of the Soret band, as well as the band in the red region.

Materials

Tetraphenylporphine was synthesized in this Laboratory by the method of Ball, Dorough and Calvin[2] and purified chromatographically by the method of Priesthoff and Banks[3] using activated alumina and Magnesol as adsorbents. The infrared spectrum of the purified material agreed with that obtained by Thomas and Martell.[4]

All acids were reagent grade and were used without further purification.

Methods

X-Irradiations were performed according to the method outlined in the previous paper,[1] using the same X-ray machine and conditions.

For gamma irradiations a Co^{60} source of approximately 1100 curies was used. Ten ml. of solution was placed in a Pyrex test tube, stoppered and irradiated in a stainless steel container at the rate of approximately 630 Kr. per hour.

All spectrophotometric measurements were made with the Model DU Beckman Spectrophotometer.

The infrared spectrum was obtained in the Perkin-Elmer, Model 21 C, double beam, recording spectrophotometer.

Results

No significant changes in the spectra were noticed upon X-irradiation of tetraphenylporphine in formic acid up to the total dose of 5000 r. On the other hand, it was found upon irradiation with much higher dosages of Co^{60} gammas that there was a decrease in the optical density of the Soret band at 436 mμ and of the band at 660 mμ. In the beginning the decrease in the optical density was proportional to the time of irradiation, but after approximately 22 minutes the optical density fell sharply (Fig. 1). At increased concentrations of tetraphenylporphine, the slope of the first portion of the curve became steeper for both bands. When the acid concentrations were reduced, the sharp drop occurred earlier. Both bands disappeared completely after 20 minutes of irradiation of tetraphenylporphine in 50% formic acid as compared to 18% decrease of both bands in 90% formic acid. The decrease of the optical density

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[2] R. H. Ball, G. D. Dorough and M. Calvin, *ibid.*, **68**, 2278 (1946).

[3] J. H. Priesthoff and C. V. Banks, *ibid.*, **76**, 937 (1954).

[4] D. W. Thomas and A. E. Martell, *ibid.*, **78**, 1338 (1956).