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

Ethyl Radical Reactions: Gamma Radiolysis of Cyclopropane in the Presence of C_2H_3T Scavenger[1]

BY H. UMEZAWA[2] AND F. S. ROWLAND

RECEIVED DECEMBER 30, 1961

The chemical alterations of C_2H_3T have been investigated during the Co^{60} gamma radiolysis of cyclopropane (700 mm.) and ethylenepropylene (0.2 to 30 mm.). The H atoms formed in radiolysis react with the olefins, and the reactions of $C_2H_4T\cdot$ radicals account for almost all of the observed changes in the radioactivity distribution. Recombination reactions with $C_2H_4T\cdot$ radicals demonstrate the presence of ethyl and isopropyl radicals from H atom reactions with olefins. The relative rate of addition to C_2H_4 and $CH_3CH{=}CH_2$ is approximately $^2/_3$. Recombination reactions also show the presence of methyl, allyl, vinyl and *n*-propyl radicals. The methyl and allyl radicals presumably are formed by the neutralization of $C_4H_8^+$ ions originating in the ion-molecule reaction, $C_3H_6^+ + C_3H_6 \rightarrow C_4H_8^+ + C_2H_4$. C_2H_5T is formed by disproportionation reactions, and leads to upper limits for the ratios of disproportionation to recombination of 0.15 ± 0.02 and 0.35 ± 0.02 for C_2H_4T with ethyl and isopropyl, respectively. Tritiated cyclopropane is also found in low yield.

Introduction

Hydrocarbon radicals are formed readily by the thermal addition of H atoms to the corresponding unsaturated molecule and are frequently formed in radiolysis systems by H atom reaction with radiation-induced olefinic impurities.[3] In appropriate systems, particular free radicals can be formed and their reactions studied through the proper choice of unsaturated scavenger. The use of radioactively labeled unsaturated molecules permits convenient tracing of the course of these reactions through the appearance of radioactivity in other identifiable chemical species.

The chemistry of the radioactive scavenger is greatly simplified if the H atom addition reaction is the only important reaction in which it is initially involved. The best choice of parent molecule for such reactions is (a) one which is a good source of H atoms under radiolysis, and (b) is itself relatively inert toward attack by hydrogen atoms and radicals. Saturated hydrocarbons, especially methane and cyclopropane, are very satisfactory in this regard. Our experiments in this series have involved the gamma radiolysis of cyclopropane in the presence of tritium-labeled ethylene, C_2H_3T.

The chemical reactions which are important in this system include all of the original radiolysis and subsequent ion-molecule reactions which lead to the product designated under

$$RH \leadsto H,\ Ri,\ Rj,\ \text{olefin, etc.} \qquad (1)$$

Some of the hydrogen atoms will add to the C_2H_3T, forming labeled ethyl radicals[4]

$$H + H_2C{=}CHT \longrightarrow CH_3\text{-}CHT\cdot \text{ or } \cdot CH_2\text{-}CH_2T \qquad (2)$$

The subsequent reactions of the $CH_2T\text{-}CH_2\cdot$ radical can include disproportionation, recombination and abstraction as illustrated in (3) to (5).

$$CH_2T\text{-}CH_2\cdot + R\text{-}\dot{C}H\text{-}CH_3 \longrightarrow CH_2T\text{-}CH_3 + R\text{-}CH{=}CH_2 \qquad (3)$$

$$CH_2T\text{-}CH_2\cdot + R\cdot \longrightarrow CH_2T\text{-}CH_2\text{-}R \qquad (4)$$

$$CH_2T\text{-}CH_2\cdot + RH \longrightarrow CH_2T\text{-}CH_3 + R\cdot \qquad (5)$$

Decomposition of the labeled radical may occur to a limited extent for other radicals but should be quite unimportant for the $CH_2T\text{-}CH_2\cdot$ radical which can decay only by loss of a hydrogen atom. The particular reactions observed in each case will depend upon the other radicals and molecules present, and will in fact serve, through the observed recombination products, to indicate the composition of the steady state radical concentration in the system during radiolysis. Appreciable control over the identity of radicals present can be exercised through the introduction of particular unlabeled scavengers and the consequent addition of H atoms to them. Variation of the olefin will single out the radicals originating by such addition. In each case, the radical contribution from the direct radiolysis, ion-molecule and ion neutralization reactions will remain.

The C_2H_3T scavenger used in these experiments furnishes a good indication of the potentialities of this technique for the study of free radical reactions in radiolysis, since many of the pertinent kinetic data are available from previous studies.

The Tritum-labeled Ethylene.—Tritium-labeled ethylene was synthesized by the catalytic addition of HT to acetylene. A mixture of T_2 and H_2 was first equilibrated with a Tesla discharge and then mixed with acetylene over a platinum catalyst for 15 hr. After reaction, the ethylene was purified by trapping at −196° of the ethylene peak effluent from a silica gel gas chromatographic column. Unirradiated duplicates of typical irradiation mixtures showed no radioactivity peak as large as 0.1% of the C_2H_3T present. Approximately 0.2 microcurie of C_2H_3T was used in each irradiated sample.

Gamma Irradiations.—Samples of cyclopropane, C_2H_3T, and unlabeled olefins were sealed in Pyrex bulbs of about 5 cc. in volume, 15 mm. i.d., equipped with break-tips. The cyclopropane was introduced first to a measured pressure; the olefins were added by condensation at −196° of the parent molecule and the ethylene or propylene from a small measured volume. The cyclopropane (Matheson) contained some propylene initially, varying with the lecture bottle used, and many of the runs were made at the propylene/cyclopropane ratio thus available.

The bulbs were irradiated along the center axis of an annular 70-curie Co^{60} source, in a radiation field of 1.4×10^5 r./hour as measured by the Fricke dosimeter. Irradiations varied from 3 hr.

---

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

[2] Japan Atomic Energy Research Institute, Tokai-mura, Japan.

[3] R. A. Back, *J. Phys. Chem.*, **64**, 124 (1960).

[4] For convenience, the further reactions will all be written for $CH_2T\text{-}CH_2\cdot$, although presumably both are formed in closely comparable amounts.

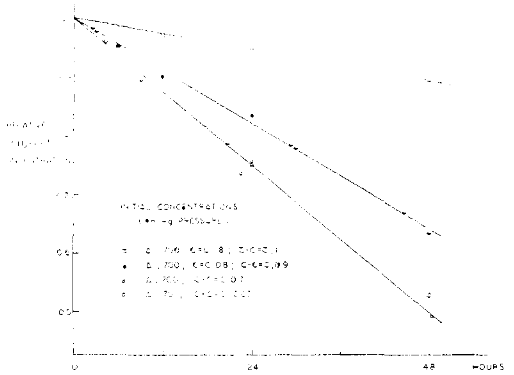


Fig. 1.—Depletion of C_2H_3T in radiolysis of cyclopropane plus C_2H_3T, C_2H_4, and $CH_3—CH=CH_2$.

to 60 hr. in duration. The temperature of irradiation was not precisely controlled but was approximately 20°.

An initial set of irradiations was conducted at 70 mm. cyclopropane pressure; the remainder of the samples contained a standard pressure of 700 mm. of parent hydrocarbon. Ethylene is formed in the 700 mm. samples at a rate of about 1.4×10^{-2} mm. pressure per hour and can be used for an estimate of the rate of cyclopropane removal. If 0.4 molecule of C_2H_4 is formed per parent molecule reacted,[5] approximately 5×10^{-3} of the cyclopropane reacts per hour. The maximum conversion then corresponds to 0.3% of the parent molecules in the longest run.

Radioactivity Assay.—The tritium activity in the various hydrocarbons after irradiation was assayed by gas proportional counting of the effluent gas from a gas chromatographic separation, as described previously.[6] One aliquot of each sample was analyzed on a 15-m. dimethylsulfolane column and another on a 3.0-m. silica gel column. Propane was added to the helium flow gas in order to obtain a gas mixture with the proper counting characteristics. The DMS column provides an excellent separation of all of the observed products except for C_2H_5T, which is barely ahead of the very large C_2H_3T peak and for which resolution is not completely satisfactory. The C_3H_7T peak follows the C_2H_3T peak closely enough on both columns to require subtraction of the tailing ethylene activity and is therefore of lesser accuracy in runs for which the total conversion of C_2H_3T to other products is small. The usual number of counts observed in each aliquot was approximately 50,000–100,000, and peaks of 50–100 counts represented the reasonable limits of detection. The percentages of "total" radioactivity are based on the sum of all radioactivities through n-$C_6H_{13}T$ (on the DMS column) as 100%.

Mass Measurements.—The macroscopic composition of the hydrocarbon mixture was determined by thermal conductivity measurements with matched thermistors prior to the addition of propane gas to the flow stream. Since aliquot sizes were not accurately measured, all mass peaks were converted to concentrations relative to the known pressure of cyclopropane. The aliquots contained sufficient cyclopropane to cause overloading of the column in each case with considerable peak-broadening. Nevertheless, the detector response for the area under the peak was directly proportional to the amount of parent hydrocarbon injected in calibration runs. The other peaks were all of normal shape and were measured by peak-height alone. The relative detector-response for each molecule was calibrated directly in terms of peak-height, except for cyclopropane, which was calibrated in terms of peak area.

Traces of ethane, propane and n-butane appeared in the mass peak measurements of the samples exposed for the longer times. These mass peaks were always quite small (<10%) compared to the olefinic concentrations.

Results

The tritium radioactivity originally present in the C_2H_3T appears in at least eight other compounds during the course of the gamma radiolysis of cyclopropane. Formation of the $CH_2T–CH_2\cdot$ radical by H atom addition to C_2H_3T will depend linearly upon the steady-state H atom concentration, and the rate of diminution of C_2H_3T activity should therefore correlate directly with the H atom concentration. The rate constants for atomic and free radical reactions under the experimental conditions are such that the H atom concentration is controlled almost entirely by the rate of reaction with olefin (see Appendix 1) and hence upon the rate of reactions[7]

$$H + C_2H_4 \xrightarrow{k_2} C_2H_5\cdot \qquad (2')$$

$$H + CH_3—CH=CH_2 \longrightarrow CH_3\text{-}\dot{C}H\text{-}CH_3 \qquad (6)$$

The rate of removal of C_2H_3T is clearly dependent upon total olefin concentration as shown in Fig. 1, in which the fraction of radioactivity remaining as C_2H_3T is plotted *versus* time of irradiation. The chemical transformation of C_2H_3T to other molecules proceeds in a manner that is approximately linear with time. Although an exponential removal might be anticipated, the steady-state H atom concentration tends to rise during these runs because of the alteration in total olefin concentration, and particularly because of the radiolytic replacement of propylene with ethylene. Consequently, all of the subsequent calculations have been performed on the approximation of a linear consumption of C_2H_3T. The numerical differences do not warrant treating the data by the more elaborate assumptions of the exponential removal plus rising steady state H atom concentration.

Five runs were carried out at a cyclopropane pressure of 70 mm., with a propylene pressure of approximately 0.07 mm. The ethylene depletion in these runs is graphed in Fig. 1. No quantitative mass measurements could be made for the olefins present under the prevailing experimental condi-

---

[5] This estimate can be made from the mass spectral pattern and ion-molecule reactions, as in B. Musgrave, Ph.D. Thesis, Univ. of Kansas, 1961.

[6] F. S. Rowland, J. K. Lee and R. Milford White, Oklahoma Conference, TID-7578, U.S.A.E.C., p. 39; J. K. Lee, *et al.*, *Anal. Chem.*, in press.

[7] The rates of reaction 2 and 2′ will be assumed identical, since the possible isotopic differences have not been measured in these experiments.

tions, and further data from these runs are not listed. Samples 12 and 14 from Table I were filled with the identical cyclopropane–propylene mixture to ten times the pressure and are shown in Fig. 1 to agree quite well with the lower pressure samples. The quantitative pattern of radioactive products is also quite similar for the two sets of pressure measurements. The close parallel in the removal of C_2H_3T for pressure differing by a factor of ten indicates that the steady-state H atom concentration is the same at the two pressures. The H atom concentration remains unchanged for the ten-fold pressure increase through simultaneous ten-fold increases in the amount of energy dissipated in the system and in the concentration of scavenger propylene molecules in the irradiation. The deposition of gamma radiation energy in the gas phase,[8] presumably largely through high energy electrons ejected from the glass walls, must therefore be proportional to the pressure of the gas in this system within a few per cent.

The composition of the gas, length of exposure and per cent. depletion of C_2H_3T are given in Table I for 23 irradiations. The product of olefin concentration and the ethylene depletion per hour has a nearly constant value, as is expected for C_2H_3T removal proportional to an H atom steady state controlled by reactions 2 and 6 exclusively. The variation from 0.008 to 0.021 (for a 130-fold change in olefin concentration) is still further reduced when two other factors involving the H atom steady-state are considered: (a) the difference in reactivity toward H atoms of C_2H_4 and $CH_3—CH═CH_2$, and (b) the reduction in H atom concentration through abstraction or other reactions at low olefin concentration. Column 7 of Table I gives the value of this product when correction is made (see below) for the differing olefinic reactivities.

The eight most abundant radioactivities observed in these experiments other than C_2H_3T are C_4H_7T-1, C_5H_9T-1, *t*-cyclopropane and five tritiated alkanes. Traces of other molecules are also found, especially in longer irradiations. No HT or CH_3T was observed in any of the runs.

The rates of formation of C_2H_5T, C_3H_7T, *t*-cyclopropane and *n*-$C_5H_{11}T$ are essentially linear with time for near-duplicate samples, as shown in Fig. 2 for the latter (Runs 55, 57, 58 and 60 in Table I). The curvature in the iso-$C_5H_{11}T$ and *n*-C_4H_9T yields is real and is readily correlated with the alteration of the unlabeled olefin concentrations by the radiolysis itself. The ethylene/propylene ratio increases with time of irradiation and is reflected in a corresponding change in the *n*-C_4H_9T/*iso*-$C_5H_{11}T$ ratio. The olefinic labeled products will also react readily with H atoms and tend toward steady-state concentrations with increasing length of irradiation.

The percentages of total observed radioactivity are also given in Table I for *n*-C_4H_9T and iso-$C_5H_{11}T$. The product of the formation rate of *n*-C_4H_9T times the olefin concentration is graphed in Fig. 3 *versus* the per cent. propylene in the olefin present during the irradiation. The average total olefin concentration has been used and the results have been plotted *versus* the olefin composition midway through the irradiation. The left tip of the triangular marks indicates the ethylene/propylene ratio at the end of the irradiation and gives an indication of the extent of alteration in the olefin composition during a run. It is quite apparent that the formation of *n*-C_4H_9T depends directly, but not linearly, upon the presence of C_2H_4 and $CH_3—CH═CH_2$ in the irradiated system and that they are formed by the recombination reaction of $CH_2T–CH_2·$ with the radicals arising from reactions 2′ and 6. The zero order rate constant (per cent. reaction per hour) has been used throughout because of the linear depletion of C_2H_3T as in Fig. 1. A similar graph, concave downwards, is obtained for iso-$C_5H_{11}T$ *versus* ethylene/propylene ratio.

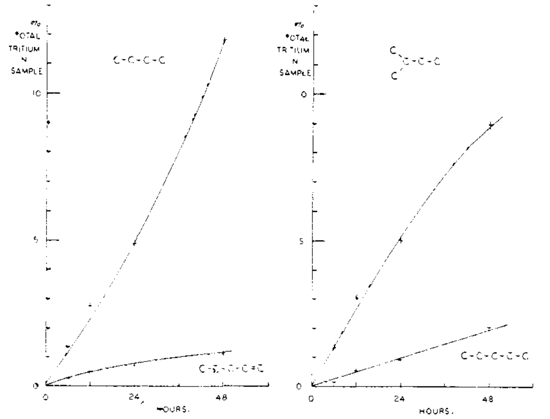


Fig. 2.—Formation of tritiated products in the radiolysis of cyclopropane in the presence of C_2H_3T, C_2H_4, and $CH_3—CH═CH_2$.

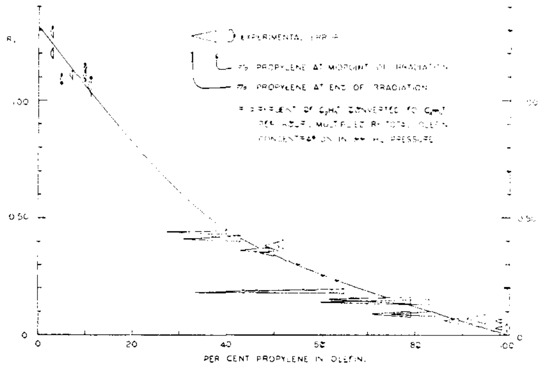


Fig. 3.—Formation of *n*-C_4H_9T in radiolysis of cyclopropane in presence of $CH_2═CHT$ and added olefins.

The deviations from straight lines arise from an inequality in the rate constants for k_2' and k_6, such that the radicals $C_2H_5·$ and iso-$C_3H_7·$ are not formed in the same ratio as that of the ethylene and propylene present. Empirical weighting of the olefin concentrations on the basis that k_2/k_6 is $^2/_3$ results in the reasonably straight lines for *n*-C_4H_9T and iso-$C_5H_{11}T$ in Fig. 4. The value of $^2/_3$ for k_2/k_6 is in excellent agreement with the recently reported value of 0.7 measured through H_2 forma-

---

[8] See, for example, A. J. Swallow, "Radiation Chemistry of Organic Compounds," Pergamon Press, Oxford, 1960.

TABLE I

Co^{60} γ-RADIOLYSIS OF CYCLOPROPANE IN THE PRESENCE OF C_2H_3T (E*), C_2H_4 (E) AND $CH_3—CH═CH_2$ (P)
(Cyclopropane pressure = 700 mm.)

Run no.	Irradiation time (hr.)	Average pressure (mm.) $\bar{E}$	$\bar{P}$	$\bar{P}/(\bar{E}+\bar{P})$	E_f^*/E_0^*	$[1-(E_f^*/E_0)]$/time (weighted olefin)	Per cent. radioactivity n-C_4H_9T	iso-$C_5H_{11}T$
12	24	0.17	0.62	0.79	0.754	0.011	4.11 ± 0.09	8.00 ± 0.12
14	48	.26	0.48	.65	.527	.010	11.8 ± .16	12.0 ± .16
25	12	.09	5.6	.98	.975	.018	0.12 ± .03	1.03 ± .05
26	40	.27	5.2	.95	.915	.017	.50 ± .05	3.91 ± .09
29	60	.45	28	.98	.969	.022	.06 ± .02	1.41 ± .06
31	40	.29	32	.99	.983	.021	.04 ± .02	0.71 ± .04
33	12	.49	0.49	.50	.854	.015	4.27 ± .10	3.95 ± .10
35	40	.58	.39	.40	.522	.014	18.0 ± .20	10.4 ± .18
36	20	9.3	.52	.05	.962	.019	2.22 ± .07	0.12 ± .04
37	40	6.0	.46	.07	.883	.019	6.92 ± .13	.62 ± .05
39	40	15.0	.49	.03	.948	.020	3.13 ± .08	.18 ± .06
40	60	14.5	.50	.03	.920	.020	5.19 ± .09	.14 ± .04
41	3	0.05	.19	.79	.892	.012	1.16 ± .05	4.07 ± .09
43	6	.11	.92	.89	.955	.011	0.33 ± .04	1.81 ± .13
44	12	.17	.88	.84	.885	.014	1.05 ± .09	4.61 ± .16
45	24	.24	.77	.76	.779	.013	3.37 ± .09	7.86 ± .14
47	24	8.7	.94	.10	.948	.022	2.74 ± .08	0.31 ± .05
48	12	7.8	.98	.11	.973	.021	1.45 ± .06	.17 ± .04
50	48	8.2	.91	.10	.893	.021	5.92 ± .12	.82 ± .06
55	6	0.82	.87	.52	.952	.017	1.37 ± .07	1.32 ± .07
57	12	.82	.84	.51	.899	.018	2.72 ± .09	3.02 ± .11
58	24	.87	.82	.49	.835	.014	4.92 ± .11	5.02 ± .11
60	48	.90	.68	.43	.636	.015	12.3 ± .13	8.96 ± .12

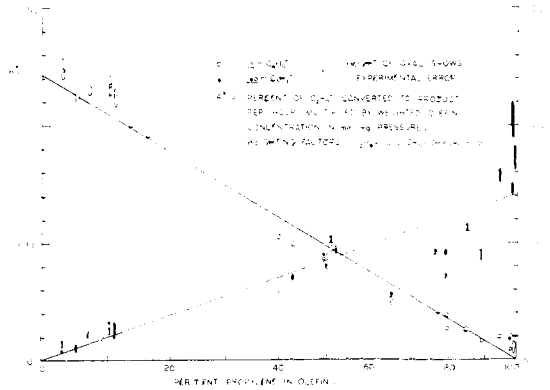


Fig. 4.—Formation of n-C_4H_9T and iso-$C_5H_{11}T$ in radiolysis of cyclopropane in presence of $CH_2═CHT$ and added olefins.

tion in scavenged radiolysis systems,[9] and with that measured by Darwent and Roberts,[10] but in complete disagreement with the value of about 5 obtained by Melville and Robb.[11] Measurements of the rate of removal of unlabeled propylene from the system were also made. The accuracy of the mass depletion measurements was not as good as the radioactivity measurements, largely because of imperfect knowledge of the original propylene pressure. Several propylene mass depletions are given in Table II for samples in which relatively accurate data are available.

TABLE II

COMPARISON OF RATES OF REMOVAL OF C_2H_3T AND $CH_3—CH═CH_2$ DURING RADIOLYSIS OF CYCLOPROPANE

Run no.	Fraction C_2H_3T removed	P_0	P_f	Fraction $CH_3—CH═CH_2$ removed	Removal ratio $\frac{CH_2═CHT}{CH_3—CH═CH_2}$
14	0.473	0.70	0.26	0.63	0.75
60	.364	.93	.44	.53	.69
44	.115	.96	.79	.18	.64

These data, within the limited accuracy of the measurements, agree with the ratio of k_2/k_6 measured above. The agreement between the two insures that no reaction other than (6), *e.g.*, abstraction of H by H atoms or radicals, is removing an important fraction of the propylene molecules that react chemically in the system.

The yield data for the other alkanes are given in Table III for the irradiated mixtures of Table I. The numbers given in the Table have been determined by multiplying the observed yield (in per cent. C_2H_3T converted to product) per hour by a weighted olefin concentration (ethylene = 1.0, propylene = 1.5). These values are very nearly constant over the large change in olefin concentration and are quite independent of the identity of the olefin involved.

The formation of labeled cyclopropane from $CH_2T–CH_2·$ is not such an obvious possibility as in the cases of the labeled saturated hydrocarbons, and the inverse dependence on the weighted olefin concentration is not necessarily expected. The yields per hour of t-cyclopropane are given in Table III and are plotted in Fig. 5 against the total olefin (unweighted) concentration. The radioactivity in cyclopropane certainly depends upon

---

[9] K. Yang, *J. Am. Chem. Soc.*, **84**, 719 (1962).

[10] B. de B. Darwent and R. Roberts, *Discussions Faraday Soc.*, **14**, 55 (1953).

[11] P. Allen, H. Melville and J. C. Robb, *Proc. Roy. Soc.* (London), **218A**, 311 (1953).

TABLE III

YIELDS FROM Co^{60} γ-RADIOLYSIS OF CYCLOPROPANE IN THE PRESENCE OF C_2H_3T, C_2H_4 AND $CH_3—CH=CH_2$

Run no.	C_2H_5T	R^{*a} C_3H_7T	n-$C_5H_{11}T$	R^{*a} C_4H_7T-1	R^{*a} C_5H_9T-1	Per cent. radioactivity per hour × 10^3 t-cyclopropane
12	0.22 ± 0.01	0.20 ± 0.01	0.06 ± 0.01	...	...	15 ± 2
14	.18 ± .01	.19 ± .01	.06 ± .01	(0.004 ± 0.001)	(0.025 ± 0.002)	18 ± 2
25	.28 ± .03	.31 ± .01	.09 ± .04	≤0.03	.19 ± 0.04	6 ± 3
26	.27 ± .02	.23 ± .02	.09 ± .01	0.02 ± 0.01	.11 ± .02	7 ± 1
29	.35 ± .04	.32 ± .03	.13 ± .04	≤0.04	.17 ± .05	5 ± 1
31	.30 ± .04	.40 ± .06	.06 ± .04	≤0.04	.20 ± .05	2 ± 1
33	.28 ± .01	.28 ± .01	.09 ± .01	...	...	17 ± 4
35	.20 ± .01	.21 ± .01	.09 ± .01	(0.004 ± 0.002)	(0.04 ± 0.01)	18 ± 2
36	.21 ± .02	.22 ± .02	.05 ± .02	.04 ± 0.02	.11 ± .03	9 ± 2
37	.20 ± .02	.22 ± .01	.08 ± .01	...	...	12 ± 1
39	.24 ± .03	.22 ± .02	.07 ± .02	.02 ± .01	.09 ± .02	7 ± 1
40	.18 ± .02	.20 ± .01	.08 ± .02	.01 ± .01	.09 ± .02	7 ± 1
41	.24 ± .01	.21 ± .01	.08 ± .01	...	...	40 ± 13
43	.24 ± .02	.17 ± .01	.08 ± .01	.01 ± .01	.06 ± .01	15 ± 6
44	.24 ± .02	.22 ± .02	.09 ± .01	...	...	23 ± 8
45	.24 ± .02	.22 ± .02	.08 ± .01	...	...	19 ± 3
47	.21 ± .02	.22 ± .02	.10 ± .02	.03 ± .01	.20 ± .03	9 ± 2
48	.22 ± .03	.27 ± .04	.11 ± .04	.03 ± .02	.06 ± .03	5 ± 3
50	.25 ± .01	.20 ± .01	.11 ± .01	...	...	11 ± 1
55	.23 ± .03	.25 ± .02	.06 ± .02	.03 ± .02	.10 ± .02	22 ± 7
57	.28 ± .02	.23 ± .01	.10 ± .01	...	...	17 ± 3
58	.23 ± .01	.22 ± .01	.08 ± .01	...	...	19 ± 3
60	.22 ± .01	.22 ± .01	.08 ± .01	...	...	16 ± 2

[a] R^* = per cent. per hour of C_2H_3T converted to tritiated product multiplied by weighted olefin concentration (E = 1.0, P = 1.5).

the concentration of unsaturated compound present, but the magnitude of the dependence is less than inverse first order.

Labeled Olefins.—The labeled olefin yields are more difficult to correlate, since these should be corrected not only for olefin concentration but also for their own depletion by H atom addition during radiolysis. It is difficult to estimate the depletion of each tritiated olefin in the absence of a measured ratio of its disappearance rate relative to that of propylene or ethylene in a similar system. Our own experiments show isobutylene[12] is removed approximately ten times faster than C_2H_3T under conditions similar to the experiments described here, indicating that the fraction of ethylene removed is not necessarily a useful correction factor for other olefins. Tritiated propylene, however, cannot be an important product, since its removal rate can be accurately estimated from the depletion of the unlabeled propylene scavenger.

The yields of C_5H_9T-1 and C_4H_7T-1 for those runs in which the C_2H_3T depletion was less than 10% are listed in Table III together with two samples (in parentheses) which showed nearly 50% conversion of C_2H_3T to other labeled forms.

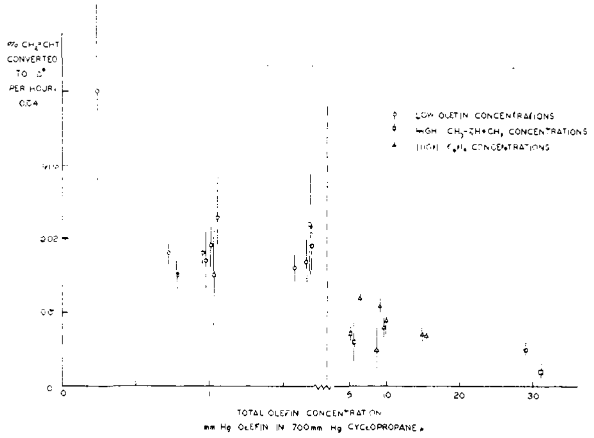


Fig. 5.—Formation of t-cyclopropane in the radiolysis of cyclopropane in the presence of $CH_2=CHT$ plus C_2H_4 and/or $CH_3—CH=CH_2$.

Discussion

Ionic Reactions.—The initial chemical reactions induced by gamma radiolysis involve the ionization of the molecules of the system and the subsequent ion–molecule and ion neutralization reactions. Although the initial stages of the chemical interactions involve this wide variety of ionic reactions, the reactions involving the tritiated chemical species are almost exclusively reactions of neutral species, *e.g.*, H atoms, free radicals, olefins, etc. This situation prevails because the ionic reactions are both rapid and relatively indiscriminate, while the parent cyclopropane is several orders of magnitude less reactive with H atoms than the olefinic scavengers in the irradiated system. The ionic reactions are thus spread over all of the molecules of the gas, while the atom reactions are all concentrated on the C_2H_3T and other olefins present.

The energy of the Co^{60} γ-radiation is deposited in the gas phase by ionization of the gas in high energy electron interactions with the molecular components. An approximate pattern of the ionization fragments to be expected in the radiolysis can be obtained from the mass spectrum observed

---

(12) H. Umezawa and F. S. Rowland, unpublished results.

about 10^{-6} second after the ionization step. However, since the fragment ions in radiolysis at one atmosphere pressure will ordinarily undergo their first collision approximately 10^{-10} second after formation, many of the initial fragment ions may not yet have dissociated to the fragments found in the mass spectrum. The ionization step affects the molecules present in the gas in proportion to the amount of each species present, weighted by the number of electrons per molecule. Labeled ethylene should thus be directly affected in ionizing reactions somewhat less rapidly than cyclopropane itself, *i.e.*, less than $5 \times 10^{-3}\%$ per hour. The actual rates of ethylene reaction per hour range from 9 to 700 times faster than this, relegating these ionizing reactions to a minor role throughout. Small effects at high olefin concentration may be measurable, however.

Ion–molecule reactions occur quite readily for many of the ions observed in mass spectrometer experiments with cyclopropane.[13] The two ions which are most prominent in the cyclopropane mass spectrum, $C_3H_6^+$ and $C_3H_5^+$, both react rapidly with the parent molecule to form C_2H_4 and $C_4H_8^+$ or $C_4H_7^+$, respectively. Since the cross sections with cyclopropane are very large, these ions should also not show any preference for reaction with the olefinic components.

The possible further reactions of $C_4H_8^+$, $C_4H_7^+$ and other ions are generally not yet known, but neutralization reactions by either electrons or negative ions (see Appendix I) will prevent the accumulation of sufficient ionic concentrations to make ion–radical reactions important.

After the ionic reactions stemming from an initial ionization are concluded, radicals and H atoms are still left and continue to react until stable molecules are formed. It is in this stage of reaction that the olefinic scavengers become heavily involved. The ionic reactions serve primarily to determine the identity of the neutral species which react with the labeled ethylene or with the labeled ethyl radical from reaction 2.

Atomic and Radical Reactions.—Concentration of all of the atomic reactions on the olefins provides information about (a) the reactions of $C_2H_4T\cdot$ radicals and about $C_2H_5\cdot$ radicals in general, (b) the identity of the radical species in the radiolysis system and semi-quantitative information about their concentrations and (c) the nature of the ionic radiolysis reactions themselves, through the reactive neutral fragments formed in them. The study of $CH_2T–CH_2\cdot$ radical reactions will become much more complicated if an appreciable fraction of the reacting $CH_2{=}CHT$ molecules does so by reactions other than (2). In particular, at low radiation dose rates, a lower steady-state radical concentration may permit radical attack on olefins as in (7) to be important

$$R\cdot + CH_2{=}CHT \longrightarrow R\text{-}CH_2CHT\cdot \qquad (7)$$

A simple approximation to the steady state kinetics of the neutral species in this system during irradiation can be made by considering only reactions 1 to 4 and 6. The numerical estimates in Appendix I demonstrate that the experiments reported here fall into a very convenient region in which the simple approximation is quite good.

$$H + RH \longrightarrow H_2 + R \qquad (8)$$

Several possible reactions, especially 5, 7 and 8 are shown to be much less important than the reactions included.

The hydrogen atom and free radical concentrations are then given by equations 9 and 10, and

$$(H)_{ss} = \frac{P_h}{k_2{}^1\,(C_2H_4) + k_6(CH_3{-}CH{=}CH_2)} \qquad (9)$$

$$(R)_{ss} = \left[\frac{P_r + P_h}{k_3 + k_4}\right]^{1/2} \qquad (10)$$

the rate of formation of $C_2H_4T\cdot$ radicals is inversely proportional to the (weighted) olefin concentration. Combination of these radicals with the radicals of (10) preserves the same dependence on olefinic concentration, in excellent agreement with the observations of Tables I and III. From the data of Appendix I, less than 2% of the C_2H_3T molecules react by paths other than H atom addition, and more than 98% of these radicals will form a stable molecule in reaction with another radical.

The lowest olefin concentrations used in these experiments are in the range for which the calculations of Appendix I indicate that some H atoms should be reacting by abstraction instead of being captured by olefin. One kinetic consequence of this is that the actual H atom steady state concentration is lower than the value calculated from (9). The data of Column 7 of Table I, which can be considered as relative measures of the H atom steady state concentrations, are plotted in Fig. 6 *versus* the weighted olefin concentration. The solid line on the graph is an approximate fit to the data on the assumption that k_8/k_2 is 9×10^{-4}. The ratio is of the right order of magnitude for H atom abstraction reactions from C_2H_6 (see appendix), whose reaction rate is similar to that of cyclopropane.[14] No other abstraction reactions should contribute substantially to (8) because of the great excess of cyclopropane, while diffusion

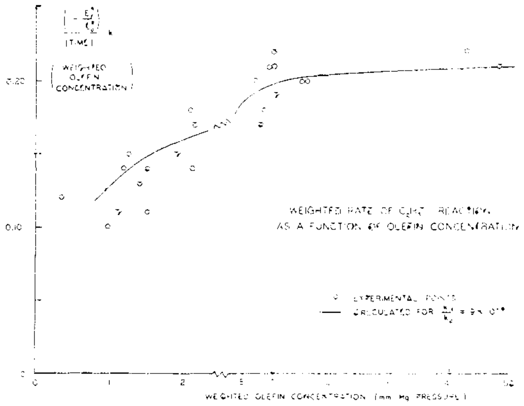


Fig. 6.—Weighted rate of C_2H_3T reaction as a function of olefin concentration.

---

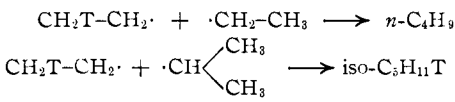
[13] R. F. Pottie and W. H. Hamill, private communication.

[14] A. F. Trotman-Dickenson, "Gas Kinetics," Buttersworth, London, 1955, p. 177.

to the walls is a minor sink for H atoms, even at low olefin concentration.[15]

Product Formation.—n-C_4H_9T, iso-$C_5H_{11}T$ and C_2H_5T. The reactions leading to n-C_4H_9T and *iso*-$C_5H_{11}T$ are the recombination reactions

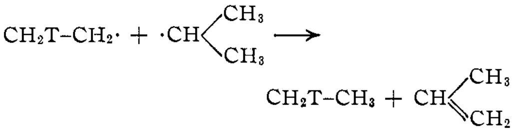
$$\mathrm{CH_2T{-}CH_2\cdot + \cdot CH_2{-}CH_3 \longrightarrow}\ n\text{-}\mathrm{C_4H_9T} \quad (11)$$



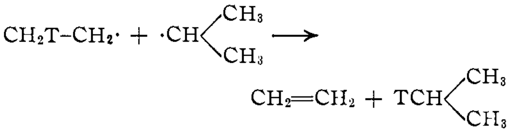
$$\mathrm{CH_2T{-}CH_2\cdot + \cdot CH}\begin{matrix}\diagup\mathrm{CH_3}\\ \diagdown\mathrm{CH_3}\end{matrix} \longrightarrow \text{iso-}\mathrm{C_5H_{11}T} \quad (12)$$

and each should be accompanied by disproportionation reactions including

$$\mathrm{CH_2T{-}CH_2\cdot + \cdot CH_2{-}CH_3 \rightarrow CH_2T{-}CH_3 + CH_2{=}CH_2} \quad (13)$$



$$\mathrm{CH_2T{-}CH_2\cdot + \cdot CH}\begin{matrix}\diagup\mathrm{CH_3}\\ \diagdown\mathrm{CH_3}\end{matrix} \longrightarrow \mathrm{CH_2T{-}CH_3 + CH}\begin{matrix}\diagup\mathrm{CH_3}\\ \diagdown\mathrm{CH_2}\end{matrix} \quad (14)$$



$$\mathrm{CH_2T{-}CH_2\cdot + \cdot CH}\begin{matrix}\diagup\mathrm{CH_3}\\ \diagdown\mathrm{CH_3}\end{matrix} \longrightarrow \mathrm{CH_2{=}CH_2 + TCH}\begin{matrix}\diagup\mathrm{CH_3}\\ \diagdown\mathrm{CH_3}\end{matrix} \quad (15)$$

Tritiated ethane can be formed by reactions 13 and 14, by similar disproportionation reactions with other radicals, and by reaction 5. If the radicals formed by H atom addition to the olefin kept some of their extra energy from the exothermic reaction through many collisions and if the abstraction or disproportionation reactions were favored by this extra energy, the yield of C_2H_5T could be substantially greater than that expected from measured disproportionation/recombination ratios.[16] Conversely, the observed ratio of C_2H_5T to n-C_4H_9T or to *iso*-$C_5H_{11}T$ is an upper limit to the ratio for k_4/k_3 of $C_2H_4T\cdot$ with $C_2H_5\cdot$ and iso-$C_3H_7\cdot$, respectively.

Table IV gives upper limits of 0.15 and 0.35 for these ratios obtained from runs high in ethylene and propylene, respectively. The latter is lower than the recent value of 0.43 given for this ratio for $C_2H_5\cdot$,[17] but both are higher than, and therefore consistent with, previous measurements of about 0.07 and 0.2 for the comparable quantities for $C_2H_5\cdot$.[18]

The additional disproportionation reaction 16

$$\mathrm{CH_2T{-}CH_2\cdot + R{-}\underset{\cdot}{C}H{-}CH_3 \longrightarrow CHT{=}CH_2 + R{-}CH_2{-}CH_3} \quad (16)$$

will show no measurable change in the radioactivity distribution.

Product Formation: C_3H_7T; Ion-Neutralization Reaction.—Small amounts of C_3H_7T can be formed from reaction 15 in the presence of isopropyl radicals,[19] but the most probable reaction for its formation is the recombination reaction as in

TABLE IV

UPPER LIMITS ON DISPROPORTIONATION/RECOMBINATION k_{13}/k_{11} AND k_{14}/k_{12}

	k_{13}/k_{11}			k_{14}/k_{12}
No.	Product ratio	Corrected for *i*-Pr contribution	No.	Product ratio
36	0.19 ± 0.02	0.17 ± 0.02	25	0.38 ± 0.04
37	.17 ± .01	.14 ± .01	26	.34 ± .02
39	.19 ± .02	.18 ± .02	29	.35 ± .04
40	.14 ± .01	.13 ± .01	31	.35 ± .04
	≤ .16 ± .02	≤ .15 ± .02		≤ .35 ± .02

$$\mathrm{CH_2T{-}CH_2\cdot + CH_3\cdot \longrightarrow CH_2T{-}CH_2{-}CH_3} \quad (17)$$

Direct comparison of the C_3H_7T and n-C_4H_9T yields indicates that the $CH_3\cdot$ concentration is about two-tenths as large as the $C_2H_5\cdot$ concentration in high ethylene concentrations. The most likely source of methyl radicals in this abundance from the radiolysis of cyclopropane seems to be the neutralization of $C_4H_8^+$ ions, as in

$$\mathrm{C_4H_8^+ + e^- \longrightarrow [C_4H_8]^* \longrightarrow CH_3\cdot + C_3H_5\cdot} \quad (18)$$

$C_3H_5\cdot$ Radicals.—The neutralization reaction 18 creates an equal concentration of $C_3H_5\cdot$ radicals of unspecified structure. Recombination of $C_2H_4T\cdot$ with allylic C_3H_5 radicals readily accounts for the formation of labeled pentene-1. A small peak ($0.02 \times C_3H_7T$) appearing at about 190 minutes on the DMS analysis corresponds to the retention time for ethylcyclopropane and represents tentative evidence for recombination with cyclic $C_3H_5\cdot$ radicals. This peak has been characterized only by its retention time on the DMS column and is not unequivocally identified.

The measured yield of C_5H_9T-1 varies more than those of the labeled alkanes, but the concentration of allylic C_3H_5 radicals seems to be within a factor of 2 or less of the methyl concentration under conditions favorable for measurement of olefin yields. Since the ratio of k_4/k_3 for allyl with $C_2H_4T\cdot$ is not known and is probably higher than for methyl with $C_2H_4T\cdot$, the unequal yields of recombination products are not unexpected.

n-$C_5H_{11}T$.—The observed rates of formation of n-$C_5H_{11}T$ indicate the presence of a moderate steady state concentration of n-propyl radicals during radiolysis; the lack of dependence of yield on olefin composition demonstrates that the radicals come from the reactions summarized as (1) and not from addition of H atoms to propylene. The mechanism of formation of the n-propyl radicals is not known.

Ions such as $C_4H_7^+$ will also be neutralized in the system and are not accounted for in terms of neutralization products. However, these ions are all relatively deficient in hydrogen and would not easily lead to $C_3H_7\cdot$ on neutralization. The subsequent reaction path of possible ionic species such as $H+$ or H_2+ is not known for this system. Similarly, it might be possible for some species of

---

(15) The r.m.s. displacement diffusing for time t is

$$\Delta = (v\lambda t)^{1/2}$$

For thermal H atoms in 700 mm. of cyclopropane and 1 mm. of C_2H_4

$v = 2.5 \times 10^5$ cm. per sec.
$\lambda = 600 \times 10^{-8}$ cm.
$1/t \cong (6 \times 10^{-14})(3.2 \times 10^{16}) \cong 2 \times 10^3$ sec.$^{-1}$

and $\Delta \leq 3$ mm.

(16) See J. C. J. Thynne, *Proc. Chem. Soc.*, 18 (1961).

(17) J. C. J. Thynne, *ibid.*, 68 (1960).

(18) P. J. Boddy and J. C. Robb, *Proc. Roy. Soc.* (London), **A249**, 547 (1959). Ignoring isotopic differences, the $C_2H_5\cdot$ plus $C_2H_5\cdot$ value of 0.12 is equivalent to 0.06 of the reaction illustrated in Table IV and 0.06 of disproportionation in the opposite direction. If T and H are equivalent, $^1/_4$ of the latter would also yield C_2H_5T, and a ratio of 0.07 is expected.

(19) If no T/H isotope effects are present in the disproportionation, the yield of (15) should be $^1/_4$ that of (16). The data of reference 18 suggest a value of no more than 0.06, probably reduced by isotope effect.

non-thermal hydrogen atoms to add to cyclopropane directly to form the radical. Such mechanisms could be consistent with the over-all requirement of inverse first power dependence on olefin concentration, but no evidence exists for or against them.

Some n-$C_5H_{11}T$ may arise from H atom saturation of labeled pentene-1 formed in (18), but normal behavior of the CH_2T–CH_2CH_2–$\dot{C}H$–CH_3 radical thus formed should include formation of iso-$C_6H_{13}T$, etc., in amounts comparable to the n-$C_5H_{11}T$ yield. The yields of such recombination products are neglible, however.

Cyclo-C_3H_5T.—The mechanism for introduction of the small amount of tritium activity into the cyclopropane molecule is not clearly shown in these experiments. Some possible explanations for the introduction of radioactivity into the parent are (a) reactions such as the capture of $\cdot CH_2\cdot$ or a similar charged species by C_2H_3T, and (b) disproportionation with cyclopropyl radicals.

Some species involved must react quite preferentially with olefins to explain the concentration dependence of Fig. 5. Although singlet methylene radicals do not show the necessary preference, the triplet radicals obtained with high argon concentrations in photolysis experiments do react primarily with double bonds and are readily scavenged by O_2 molecules.[20]

Comparison of similar runs carried out at 70 and 700 mm. of cyclopropane indicates that only about half as much *cyclo*-C_3H_5T relative to other products is formed in the lower pressure irradiations as in the higher. Other relative yields are approximately the same (±20%) for both pressures. Since the runs on which such comparisons can be accurately made for *cyclo*-C_3H_5T, all have heavy depletion of C_2H_3T and $CH_3CH{=}CH_2$, the yield of tritiated propylene is quite difficult to measure, and the significance of the pressure variation has not yet been ascertained.

The exchange reactions of CH_2T–$CH_2\cdot$, such as disproportionation, should have an inverse first order dependence upon olefin concentration, a stronger dependence than actually observed. Further experiments will be required to determine the exact mechanisms involved in the *cyclo*-C_3H_5T formation. Experiments with $CH_2{=}C^{14}H_2$ as the radioactive scavenger can distinguish readily between the two classes of mechanism given above.

Relative Concentrations of Free Radicals During Irradiation.—The intercept for n-C_4H_9T in Fig. 4 is higher than that for *iso*-$C_5H_{11}T$, implying that $k_{11} > k_{12}$ by a factor of about 1.5. This can be qualitatively correlated with the higher percentage of disproportionation reactions expected for sec-alkyl as compared to n-alkyl radicals.[21] The relative steady state concentrations of radicals are estimated in Table V for the two limits of olefinic composition.

The concentrations given in Table V, after correction for disproportionation to C_2H_5T and back to C_2H_3T, should still be weighted further by the relative values of k_4 for each. Most of these values are not known, so the relative free radical concentrations of Table V are only semi-quantitative. The disagreement between the values for iso-C_3H_7 and $C_2H_5\cdot$ under conditions such that all H atoms should be olefin scavenged could arise from just such a difference in k_4 rate constants.[22]

TABLE V

RELATIVE FREE RADICAL CONCENTRATIONS IN SYSTEM DURING CYCLOPROPANE GAMMA RADIOLYSIS

Scavenger radical	Propylene: Product ratio	Propylene: Corrected for disproport.[21]	Ethylene: Product ratio	Ethylene: Corrected for disproport.[21]
$\cdot CH_3$	0.30 ± 0.03	0.32	0.30 ± 0.03	0.32
$\cdot CH_2$—CH_2—CH_3	.10 ± .02	.11	.10 ± .02	.11
$\cdot CH_2$—$CH{=}CH_2$	.16 ± .03	.16	.14 ± .03	≥.14
$\cdot CH{=}CH_2$	.03 ± .02	.03	.02 ± .01	≥.02
$\cdot CH(CH_3)_2$	1.00	1.5	...	...
$\cdot CH_2CH_3$	...	...	1.8	2.0
Ethane	0.32 ± 0.02		0.28 ± 0.03	

Acknowledgment.—We wish to acknowledge frequent discussions with Dr. Burdon Musgrave concerning cyclopropane radiolysis.

Appendix 1

Approximate Steady State Kinetics of the System during Radiolysis. A. Free Radical Processes. The steady state treatment of the set of equations

$$RH \xrightarrow{\sim\sim} H,\ Ri,\ Rj,\ \text{olefin, etc.} \qquad (1)$$

$$H + CH_2{=}CHT \longrightarrow CH_2T{-}CH_2\cdot \qquad (2)$$

$$H + CH_2{=}CH_2 \longrightarrow CH_3{-}CH_2\cdot \qquad (2')$$

$$H + CH_3{-}CH{=}CH_2 \longrightarrow CH_3{-}\underset{\cdot}{C}H{-}CH_3 \qquad (6)$$

$$R + R \longrightarrow R{-}R \text{ or} \qquad (4)$$

$$\text{disproportionation} \qquad (3)$$

gives the concentration of H atoms as

$$(H)_{ss} = \frac{P_h}{k_2'\,(C_2H_4) + k_6\,(CH_3{-}CH{=}CH_2)} \qquad (9)$$

and the radical concentration as

$$(R)_{ss} = \left[\frac{P_r + P_h}{(k_3 + k_4)}\right]^{1/2} \qquad (10)$$

P_h and P_r are the total production rates of hydrogen atoms and radicals, respectively, from all of the ionization, ion-molecule and ion-neutralization reactions summarized in equation 1. Semi-quantitative values for $(H)_{ss}$ and $(R)_{ss}$ can be estimated from the observed rate of formation of ethylene (0.002% of cyclopropane concentration per hour, or 1.3×10^{11} molecules per cm.^{3} per sec.). P_h is somewhat greater than the ethylene production rate, and an estimate of 1.8×10^{11} atoms per cm.^{3} per second is obtained using the relative H/C_2H_4 yields calculated by Musgrave.[5] The contribution of P_r to the total radical production rate is difficult to estimate, since it requires knowledge of the ion-neutralization reactions; $(P_h + P_r) \sim 2.5 \times 10^{11}$ radicals per cm.^{3} per second is a reasonable approximation. The calculated values at 10 mm. pressure of C_2H_4 are $(H)_{ss} = 9 \times 10^6$ atoms/cm.^{3} and $(R)_{ss} = 7 \times 10^{10}$ radical/cm.^{3}, using the values listed at the end of the Appendix.

This simplified kinetic analysis assumes that several other reactions are unimportant relative to those given above. The most important of these limitations is that the ratios below should all be >>1. Approximate numerical estimates are made for cyclopropane (700 mm.) and ethylene (10 mm.) under these radiolysis conditions.

---

(20) H. M. Frey, *J. Am. Chem. Soc.*, **82**, 5947 (1960).

(21) J. N. Bradley, *J. Chem. Phys.*, **35**, 718 (1961).

(22) The C_2H_3T consumption of Table I is less than the rate of formation of $C_2H_4T\cdot$ to the extent that reactions such as (16) return the radical to the original ethylene. This deficit is greater for reactions with iso-$C_3H_7\cdot$ radicals than for $C_2H_5\cdot$, but the relative error in this comparison is only about 10%. The absolute deficit cannot be calculated until the k_4's are known for allyl and any other radicals in the system.

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

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

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

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

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

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

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

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

---

(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

RECEIVED JANUARY 2, 1962

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, $Li^6(n,\alpha)T$ or $He^3(n,p)T$. 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%. 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

---

(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**, 1867 (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).