ISOTOPIC AND HOT RADICAL EFFECTS IN THE REACTION OF HYDROGEN ATOMS WITH ETHYLENE[1]

A. H. TURNER[2] AND R. J. CVETANOVIĆ

ABSTRACT

Reactions of D atoms with C_2H_4, H atoms with C_2D_4, and H atoms with C_2H_4 at room temperature are compared. Pronounced differences in the extent of isotopic exchange have been found. The observed isotopic and pressure effects provide evidence for the importance of "hot" ethyl radicals in these reactions and their responsibility for isotopic exchange. The atoms are generated by the mercury-photosensitized decomposition of hydrogen and deuterium and their concentration is sufficiently small so that "atomic cracking" does not occur.

INTRODUCTION

Addition of a hydrogen atom to a molecule of ethylene leads to the formation of an energy-rich ethyl radical. The need to take into account the formation and subsequent reactions of such "hot" ethyl radicals in order to explain and reconcile seemingly divergent experimental information from various sources has been recently stressed by Bradley, Melville, and Robb (1).

In the present work additions of H and D atoms, respectively, to ethylene have been compared at various pressures. Similar systems have been recently studied by Toby and Schiff (2) but at very low pressures and at high atom-to-ethylene ratios so that "atomic cracking" was favored and methane was the main product, with only smaller amounts of ethane and ethylene and traces of butane and propane. In contrast to this in the present work the ratio of concentrations of the atoms and ethylene has been sufficiently small so that atom–radical reactions have been negligible and the only observed products are butane, ethane, and ethylene, resulting from combination and disproportionation of ethyl radicals.

From the observed effect of pressure on the amounts and isotopic structure of products, direct evidence has been obtained for the important role of "hot" ethyl radicals in these reactions as well as for their responsibility for the occurrence of isotopic exchange. The reactions have been carried out at room temperature where attack of thermalized free radicals on H_2 or D_2 is too slow to be of importance. In view of the difference in the strengths of CD and CH bonds an isotopic effect has been anticipated, and it has been found that isotopic exchange occurs when D atoms add to C_2H_4 but not when H atoms add to C_2D_4. As a result the *course* of the reaction in the two cases is quite different. Some information on the mechanism of disproportionation of ethyl radicals has also been obtained.

EXPERIMENTAL

A conventional high vacuum apparatus was used with a cylindrical quartz reaction cell 5 cm in diameter and 10 cm long. Mercury resonance radiation was obtained from a low pressure mercury arc situated some 20 cm from the reaction cell and was roughly collimated with a highly polished aluminum cylinder.

Research grade ethylene was employed and hydrogen was purified by passage through a heated palladium thimble. Tetradeuteroethylene, at least 99 atom % pure, was kindly supplied by Dr. L. C. Leitch of these laboratories.

---

[1] *Manuscript received February 27, 1959.*
Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada.
Issued as N.R.C. No. 5187.

[2] *National Research Council Postdoctorate Fellow 1955–57. Present address: Carrington Research Laboratory, Petro-Chemicals Limited, Urmston, Manchester, England.*

Can. J. Chem. Vol. 37 (1959)

RESULTS

All experiments were performed at room temperature and the results for H + C_2D_4, D + C_2H_4, and H + C_2H_4 are given in Tables I, II, and III, respectively. Large excess of hydrogen (or deuterium) and very small amounts of ethylene were used. This ensured essentially quantitative quenching of the Hg $6(^3P_1)$ atoms by hydrogen and also made feasible mass spectrometric analyses of the recovered C_2 hydrocarbons without necessitating excessively long exposures.

Butanes and C_2 hydrocarbons were condensed in liquid nitrogen and, after the unreacted excess hydrogen was pumped off, were separated by a LeRoy still (3), measured with a constant volume gas burette, and then analyzed by mass spectrometry. No products other than those shown in the tables were detected. The observed mass balance was usually slightly below 100%, in all probability due to the difficulty of quantitatively recovering C_2 hydrocarbons from the large excess of hydrogen employed. For this reason, besides the values actually observed for ethylene and ethane, the "corrected" values are also given in the Tables I–III. The latter were calculated by assuming complete recovery of butane and scaling up the C_2 fraction to obtain 100% carbon atom balance. The amount of the C_2 fraction was, therefore, assumed to be equal to the original ethylene less twice the amount of the recovered butane. The relative proportions of ethylenes and ethanes were then calculated from the mass spectrometric analyses of the recovered C_2 fraction. In general, these corrections were not particularly large.

The mass spectrometric analyses were subject to the usual uncertainties in the values of the lighter constituents, especially when they were formed in very small amounts, because of cumulative errors in the corrections for the fragment peaks of the heavier constituents present.[3] Thus in Table I, in addition to the two ethanes, C_2D_5H and $C_2D_4H_2$, some $C_2D_3H_3$ is also indicated. However, the analytical uncertainty for this compound is so high that it is not certain whether it is formed at all and it has, therefore, been omitted from the table. Similarly, the figures for C_2D_3H are only approximate. The ratio of C_2D_5H and $C_2D_4H_2$, on the other hand, should be reliable. The C_4 fraction consists in this case of essentially pure $C_4D_8H_2$ (with less than 0.3% of d_9 and d_{10} butanes) and the indications are that the two H atoms are on the terminal carbon atoms. In Table II the figures for C_2H_4, C_2H_3D, C_2H_6, and C_2H_5D are probably not too accurate and, similarly, in the C_4 fraction the figures for C_4H_{10} are not too reliable.

TABLE I

Products of the reaction H + C_2D_4 (25±1° C; exposure 60 minutes; "corrected" values are in italics)

Run	P_{H_2}, mm	C_2D_4 Taken, µmoles	Products (micromoles)					$(C_2D_5H + C_2D_4H_2)$	C_2D_4 Consumed, µmoles
			C_2D_4	C_2D_3H	C_2D_5H	$C_2D_4H_2$	$C_4D_8H_2$	$(C_4D_8H_2)$	
Q3	51.3	87.0	56.92	0.69	0.40	1.40	12.0	0.150	
			60.3	*0.73*	*0.42*	*1.48*		*0.158*	*26.7*
Q2	99.5	87.0	55.68	0.68	0.41	1.23	13.0	0.126	
			58.1	*0.71*	*0.43*	*1.28*		*0.132*	*28.9*
Q1	299.7	87.3	56.99	0.63	0.44	0.88	13.6	0.097	
			57.7	*0.64*	*0.45*	*0.89*		*0.099*	*29.6*

---

[3] *The mass spectra of the deutero compounds from the American Petroleum Institute catalog of mass spectral data were used where available. In other cases estimates of probable fragment intensities were made by analogy with the known spectra.*

TABLE II

Products of the reaction D + C_2H_4 (25±1° C; exposure 60 minutes in $M_{8,\,9,\,10}$, 120 minutes in $M_{6,\,7}$; initial C_2H_4 88.5 micromoles in all experiments; "corrected" values are in italics)

Run	P_{D_2}, mm	Products (micromoles)											C_2H_4 Consumed, μmoles
		C_2H_4	C_2H_3D	C_2H_6	C_2H_5D	$C_2H_4D_2$	$C_2H_3D_3$	C_4H_{10}	C_4H_9D	$C_4H_8D_2$	$C_4H_7D_3$	Total butane	
M_{10}	49.3	51.7	4.61	4.23	1.81	—	—	0.82	3.28	4.55	0.52	9.17	
		58.3	*5.20*	*4.78*	*2.04*	—	—						*30.2*
M_9	99	36.9	5.83	4.37	1.46	—	—	0.67	3.17	5.29	0.43	9.56	
		52.7	*8.35*	*6.25*	*2.09*	—	—						*35.8*
M_8	300	55.4	3.07	4.10	1.71	—	—	0.33	1.78	8.07	0.33	10.51	
		58.3	*3.23*	*4.31*	*1.80*	—	—						*30.2*
M_6	300	23.9	2.36	4.55	2.98	1.0	0.06	0.82	4.30	17.1	1.73	23.95	
		27.7	*2.73*	*5.25*	*3.43*	*1.4*	*0.07*						*60.8*
M_7	606	21.7	1.76	2.52	2.23	1.12	—	0.95	3.33	20.25	1.05	25.58	
		27.4	*2.23*	*3.19*	*2.82*	*1.42*	—						*61.1*

The analytical uncertainties preclude a detailed quantitative analysis of the pressure dependence of the investigated reactions and for this reason no attempt has been made at present to accumulate more extensive experimental data. Fortunately, the values for the major products formed are in general reasonably reliable. There can, as well, be little doubt of the reality of the general trends observed and in particular of the pronounced difference in the complexity of the products shown in Tables I and II, respectively. As a result a number of conclusions can be safely drawn.

DISCUSSION

A significant result of the present work is the finding that isotopic exchange takes place readily when D atoms add to C_2H_4, even at relatively high pressures of D_2, while there is no exchange when H atoms add to C_2D_4. In the former case the formation of different isotopic butanes indicates, besides C_2H_4D radicals, the presence of C_2H_5 and $C_2H_3D_2$ radicals as well. In the latter case, on the other hand, only C_2D_4H radicals are present.

The amount of isotopic exchange in the reaction of D atoms with C_2H_4 (Table II) increases at lower pressures of D_2 and the following reactions have, therefore, to be considered:

$$C_2H_4 + D \rightarrow C_2H_4D^* \qquad [1]$$

$$C_2H_4D^* \rightarrow C_2H_3D + H \qquad [2]$$

$$\left[\text{or} \quad C_2H_4D^* + C_2H_4 \rightarrow C_2H_3D + C_2H_5^* \qquad [2a]\right]$$

and

$$C_2H_4D^* + M \rightarrow C_2H_4D + M \qquad [3]$$

with subsequent reactions of the H atoms produced in reaction [2] and recombination and disproportionation of the ethyl radicals formed. Addition of H atoms to the original ethylene, C_2H_4, produces C_2H_5 and as the conversion increases, D atoms will add to C_2H_3D formed in reaction [2] to give increasing amounts of $C_2H_3D_2$. The observed trends with pressure and over-all conversion in the amounts of various butanes formed in the reaction of D atoms with C_2H_4, as shown in Table II, are in qualitative agreement with the indicated reactions.

In the reaction of H atoms with C_2D_4 (Table I) the only equivalent of reaction [2] which occurs is

$$C_2D_4H^* \rightarrow C_2D_4 + H \qquad [4]$$

$$\left[\text{or} \quad C_2D_4H^* + C_2D_4 \rightarrow C_2D_4 + C_2D_4H^* \qquad [4a]\right]$$

but not

$$C_2D_4H^* \rightarrow C_2D_3H + D \qquad [5]$$

$$\left[\text{nor} \quad C_2D_4H^* + C_2D_4 \rightarrow C_2D_3H + C_2D_5^*. \qquad [5a]\right]$$

No isotopic exchange is therefore observed.

The difference between the two cases is readily understandable in view of the difference in the bond dissociation energies between a C–D and a C–H bond as a result of the difference in the zero point energies. When a H atom adds to C_2D_4, the hot $C_2D_4H^*$ radical possesses enough excess energy to undergo reaction [4] but not reaction [5]. When a D atom adds to C_2H_4, on the other hand, the hot $C_2H_4D^*$ radical formed possesses enough excess energy to split off a D or a H atom, and both the statistical and the energetic conditions favor the latter (reaction [2]).

The isotopic structure of the ethanes formed and the pressure effects observed in these experiments are of interest from the point of view of "disproportionation" of ethyl radicals. Under conditions of the present work, ethane could not have been formed by combination of methyl radicals because if this were so appreciable quantities of propane would have been formed as well and this was not the case. Reaction of H atoms with C_2D_4 is relatively simple and the analytical results in Table I for the two ethanes formed, C_2D_5H and $C_2D_4H_2$, are reasonably reliable. (Some $C_2H_3D_3$ might have been produced as well but this is highly uncertain.) C_2D_6 is not formed. These results are not inconsistent with the "head-to-tail" disproportionation mechanism of Wijnen and Steacie (4). The ratio $C_2D_4H_2/C_4D_8H_2$ increases at lower pressures while the ratio of $C_2D_5H/C_4D_8H_2$ is pressure-independent. The following reactions ought then to be considered:

$$C_2D_4H + C_2D_4H \rightarrow C_2D_5H + C_2D_3H \qquad [6]$$

$$C_2D_4H + C_2D_4H \rightarrow C_2D_4H_2 + C_2D_4 \qquad [7]$$

$$C_2D_4H^* + C_2D_4H \rightarrow C_2D_4 + C_2D_4H_2^* \qquad [8]$$

$$C_2D_4H_2^* + M \rightarrow C_2D_4H_2^* + M. \qquad [9]$$

Reactions [6] and [7] involve thermalized radicals and lead, therefore, to a pressure-independent ratio of $C_2D_5H/C_4D_8H_2$. Reaction [8] explains the increase in $C_2D_4H_2$ as the pressure is lowered. It appears therefore necessary to assume that under the conditions employed in these experiments an H atom is abstracted much more readily than a D atom from a hot C_2D_4H radical in spite of the more favorable statistical ratio of D atoms. It is unlikely that $C_2D_4H_2$ was formed by addition of H atoms to C_2D_4H since, if anything, the pressure dependence would then be opposite to that observed.

In contrast to the results obtained in the present work, Dills and Rabinovitch (5) obtained a more complex isotopic structure of the products in an experiment with C_2D_4 and H atoms at a total pressure of about 4 mm, using a simulated point source (nozzle) of H atoms, and maintaining a spherical diffusion reaction zone. The butanes consisted of $C_4D_8H_2$ (83%), C_4D_9H (15%), and C_4D_{10} (2%) and the ethanes of C_2D_6 (63%), C_2D_5H (18%), and $C_2D_4H_2$ (19%). This was interpreted to show that the mechanism of disproportionation is not "head-to-tail" but rather that the disproportionation takes place with more than one atom migrating. This conclusion cannot be of general validity since C_2D_6, C_4D_9H, and C_4D_{10} are not formed in the same reaction under conditions employed in the present work in which the products formed are consistent with a "head-to-tail" disproportionation. The more complex isotopic structure of the butane and ethane obtained by Dills and Rabinovitch appears to be due to the particular conditions employed by these authors and the reason for the greater complexity is not quite clear. Perhaps at very low pressures some exchange involving transfer of D atoms does occur. Since reaction [5] is slightly endothermic while [5*a*] is exothermic, the latter would perhaps provide the more readily acceptable mechanism of such an exchange. However, further experimental information is necessary before any firm conclusions can be drawn.

In the reaction of D atoms with C_2H_4 (Table II) no $C_2H_4D_2$ is formed at low conversions, and the disproportionation of C_2H_4D radicals (including also the reactions involving $C_2H_4D^*$) is, therefore, entirely by abstraction of a hydrogen atom.

$$C_2H_4D + C_2H_4D \rightarrow C_2H_5D + C_2H_3D \tag{10}$$

$$C_2H_4D + C_2H_4D^* \rightarrow C_2H_5D^* + C_2H_3D \tag{11}$$

$$C_2H_5D^* + M \rightarrow C_2H_5D + M \tag{12}$$

Abstraction of hydrogen atoms is here favored both statistically and energetically. Only at higher conversions $C_2H_4D_2$ is formed as a result of the eventual addition of D atoms to C_2H_3D produced in the course of the reaction. Formation of C_2H_6 is a consequence of the readily occurring isotopic exchange (reaction [2] or [2*a*]).[4]

A striking feature of the results of the performed experiments is the fact that the isotopic exchange (reactions such as [2] or [2*a*]) and the "hot radical" effects in the disproportionation (reactions such as [8] and [11]) persist to quite high H_2 or D_2 pressures. The occurrence of reactions such as [2] at high pressures could be explained by assuming very short natural lifetimes of the energy-rich radicals and perhaps, as is frequently done, a very readily occurring deactivation by collision for this particular process. The occurrence of reactions such as [8] and [11], on the other hand, must mean that the energy-rich ethyl radicals are deactivated in collisions only extremely slowly and are capable of undergoing preferential disproportionation (and exhibiting as well a strong isotopic effect in disproportionation), even after undergoing numerous collisions in the gas phase with H_2 or D_2 and with ethylene. Thus, for example, although in the reaction of H atoms and C_2D_4 the ratio of the concentrations of hydrogen at a pressure of 100 mm and C_2D_4H (calculated approximately from the rate of formation of $C_4D_8H_2$) is of the order of 10^5 to 10^6, there are still pronounced isotopic and pressure effects in the formation of ethane. Similarly, the pressure dependence of the ratio of disproportionation to combination in the reaction of H atoms with C_2H_4 (Table III) persists to quite high hydrogen pressures.

TABLE III

Products of the reaction H + C_2H_4 (25±1° C; exposure 60 minutes; "corrected" values are in italics)

Run	P_{H_2}, mm	C_2H_4 Taken, µmoles	Products (micromoles)			C_2H_4 Consumed, µmoles	C_2H_6/C_4H_{10}
			C_2H_4	C_2H_6	C_4H_{10}		
M_5	101	88.0	53.4	3.44	12.6		
			59.5	*3.77*		*28.5*	*0.30*
M_1	300	88.9	46.6	2.28	15.0		
			56.7	*2.79*		*32.2*	*0.19*
M_4	616	87.8	51.3	2.36	16.6		
			52.9	*2.40*		*34.9*	*0.14*

[4] *Since all ethane results from disproportionation of ethyl radicals, the relative abundance of* C_2H_6 *and* C_2H_5D *depends on the relative importance of reactions [2] (or [2a]) and [3], respectively. In the limiting case when reaction [3] is negligible, i.e. as pressure tends to zero, all the ethane would consist of* C_2H_6 *(as long as the conversion is small, i.e. until appreciable quantities of* C_2H_3D *are accumulated).*

In principle, it might appear to be possible to obtain quantitative information on the lifetimes of the "hot" radicals from a study of the pressure dependence of the yields of the products. The somewhat limited experimental information on pressure effects obtained in the present work and the limitations in analytical accuracy preclude a detailed analysis of this kind. However, the data in Tables I–III appear not to be consistent with the postulates of single hot radical species the rate of deactivation of which depends linearly on pressure.

The finding that abstraction of a hydrogen atom from a hot ethyl radical takes place very readily and that when the hot radical contains both H and D atoms it is the former which are abstracted, makes it necessary, by analogy, to consider the reactions of the type [2*a*] and [4*a*] as the ones which may perhaps be responsible for the isotopic exchange. However, on the basis of the available information the two types of processes (reactions [2] and [4] as contrasted with [2*a*] and [4*a*]) cannot be differentiated. Whether reactions of the latter type occur or not should perhaps be possible to establish by producing hot C_2H_5 radicals from photolysis of mercury diethyl in the presence of C_2D_4.

The ambiguity between these two types of processes may be rather general for exchange reactions of similar kind. Thus, the isotopic exchange and deuterium atom enrichment in the methane formed in the reaction of ethylene (2) or ethane (6), under conditions where atomic cracking takes place, may be due to the reactions of the type

$$CH_3 + D \rightarrow CH_3D^* \qquad [13]$$

$$CH_3D^* \rightarrow CH_2D + H \qquad [14]$$

$$CH_3D^* + M \rightarrow CH_3D + M \qquad [15]$$

as is generally assumed (6), or instead of [14]

$$CH_3D^* + R \rightarrow CH_2D + RH^*, \qquad [14a]$$

where R is D, an ethyl or a methyl radical and RH* may still be to some extent "hot", since the excess energy would be expected to be predominantly transferred into the product (RH*) in which a bond is formed. (Energetically the process simulates to a large extent the sequence of reaction [14] followed by combination of H and R to give RH*.)

Recently Lavrovskaia *et al.* (7) have proposed the following reaction as the one responsible for isotopic exchange in free radical reactions of hydrocarbons:

$$RCH_2\cdot + D_2 \rightarrow RCHD\cdot + HD. \qquad [16]$$

However, we find[5] no isotopic exchange at room temperature between thermalized ethyl radicals (from photolysis of diethyl ketone) and D_2 or C_2D_4. Reactions of this type, therefore, do not occur under conditions of the present experiments and are in general not likely to be important when thermalized radicals are involved.[6] Whether such reactions may occur when the free radicals are "hot" cannot be said at present. In such a case reaction [16] would become analogous to reaction [2*a*], tentatively suggested as a possibility in the present work.

ACKNOWLEDGMENT

The authors are grateful to Dr. A. W. Tickner for mass spectrometer analyses and their interpretation.

---

[5] *The authors are grateful to Mr. S. Sato for performing these experiments.*
[6] *Reaction [16] is also discussed in reference (6).*

REFERENCES

1. Bradley, J. N., Melville, H. W., and Robb, J. C. Proc. Roy. Soc. A, **236**, 318 (1956).
2. Toby, S. and Schiff, H. I. Can. J. Chem. **34**, 1061 (1956).
3. LeRoy, D. J. Can. J. Research, B, **28**, 492 (1950).
4. Wijnen, M. H. J. and Steacie, E. W. R. Can. J. Chem. **29**, 1092 (1951).
5. Dills, D. H. Lifetimes for decomposition of vibrationally excited dideuteroethyl radicals. Ph.D. Thesis, University of Washington. 1956.
6. Berisford, R. and LeRoy, D. J. Can. J. Chem. **36**, 983 (1958).
7. Lavrovskaia, G. K., Mardaleishvili, R. E., and Voevodskii, V. V. Voprosy Khim. Kinetiki, Kataliza, i Reakstsionnoi Sposobnosti, Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 40 (TT-701) (1955).