determined by X-ray diffraction methods.[9,10] Moreover, the directions of the minimum principal values of protons H_2 and H_2' form an angle of 60° with each other, thus indicating a *cis*-configuration for the two C–H bonds in the radical. This, in turn, confirms a *cis*-structure for the parent molecule, assuming that no violent change in the orientation of the molecule occurs during the irradiation.

If the two C–H bonds in the radical were to have a *trans*-relationship to each other, the angle between the directions of the 6 Mc. values of H_2 and H_2' would have been close to 0°. In fact, the directions of all the principal values of H_2 and H_2' would have been very nearly parallel to each other. In such a case, the e.m.r. spectrum shown in Fig. 2C, in which the splitting due to one proton is 22.5 Mc. and that due to the other is 12.5 Mc., could not have occurred.

Arguments similar to the ones presented here were utilized previously in the study of the structure of an allyl-type radical $HOOC–CH{=}CH–\dot{C}H–COOH$ found in X-irradiated glutaconic acid, $HOOC–CH{=}CH–CH_2–COOH$. In that case, the e.m.r. results have established that the stable isomer of glutaconic acid is the *trans*-isomer.

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The Secondary Deuterium Effect in CH_3 and CF_3 Addition Reactions

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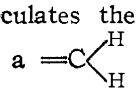
The secondary deuterium effect was investigated for the CH_3 and CF_3 addition reactions. The results obtained for the relevant k_D/k_H were

$CD_2{=}CD_2$	1.05 for CH_3, 1.07 for CF_3	$PhCD{=}CD_2$	1.11 for CH_3, 1.10 for CF_3
$CH_3CH{=}CD_2$	1.12 for CH_3, 1.07 for CF_3	$CD_2{=}CDCD{=}CD_2$	1.20 for CH_3, 1.09 for CF_3
$CD_3CD{=}CD_2$	1.17 for CH_3, 1.09 for CF_3		

It is concluded that the incipient CH_3 (or CF_3)–C bonds in the respective transition states are relatively long, and that the remaining groups around the reactive center retain their original planar configuration. This conclusion does not appear to be invalidated by the recent argument of Wolfsberg.

The addition of a radical R to an olefinic or aromatic molecule A yields an adduct radical, as shown by the equation $R\cdot + A \rightarrow RA\cdot$. The relative rate constant of the addition process k_2 may be related to the atom localization energy of the most reactive center of the substrate. For example, in the addition of CH_3 radicals to aromatic non-substituted hydrocarbons, a linear relation was observed for $\log(k_2/n)$,—n being the number of reactive centers— and the respective atom localization energy.[1] Such a relation was previously reported for the addition of CCl_3 radicals to aromatic hydrocarbons[2] and more recently for the CF_3 radical addition to the same series of substrates.[3] A linear relation between the rate constant and localization energy was also observed for the addition of CH_3 radicals to ethylene, styrene, butadiene, vinyl naphthalene, etc.[4,5] The existence of such relations was interpreted as an indication of the formation of an incipient, covalent R–C bond in the transition state of the addition.

The formation of an incipient bond between the radical R and the reactive carbon center of the substrate eventually leads to a rearrangement around this center; *i.e.*, its original planar trigonal configuration is transformed into a tetrahedral one. The question arises, however, to what extent does such a change take place in the transition state. If the incipient R–C bond is relatively long, the configuration of the other groups around the reaction center should remain planar, but if its length approaches that characterizing the C–R of the final state, then the configuration in the transition state will be tetrahedral.

In order to get some information pertinent to this problem, we decided to investigate the secondary deuterium effect in the radical addition reaction. It was pointed out by Streitwieser[6,7] that the relatively soft out of plane C–H vibration of a trigonal carbon is transformed into a harder bending vibration in a tetrahedral carbon. For such a change, one calculates the ratio k_D/k_H for a reaction involving a  $=C\begin{smallmatrix}H\\H\end{smallmatrix}$ center to be 1.82 at 65°. One may expect, therefore, that a value of k_D/k_H close to unity would indicate a planar transition state and a long R–C bond, whereas if k_D/k_H is close to 1.82, the configuration around the reactive center in the transition state should be essentially tetrahedral.

The first attempt to utilize this technique for the study of the transition state of radical addition reactions was reported by Matsuoka and Szwarc.[8] They determined the k_D/k_H ratio for the addition

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TABLE I

k_2, rate constant of the addition reaction $R\cdot + A \longrightarrow RA$ and k_1, rate constant of the reaction $R\cdot$ + isoöctane $\longrightarrow$ RH + isoöctyl radical. Solvent, isoöctane; T, 65°, radicals produced by photolysis of azo compounds RN=NR; [RN=NR] $\approx 10^{-3}$ M.

Substrate	Mole % of substrate	$m16/m28$	k_2/k_1
	Addition of CH_3 radicals		
....	0	0.5418	..
....	0	.5420	..
$CH_2{=}CH_2$	2.72	.2662	38.2
$CH_2{=}CH_2$	2.72	.2635	39.0
$CH_2{=}CH_2$	2.72	.2673	38.9
		Av.	38.35 ± 0.4
$CD_2{=}CD_2$	2.72	.2586	40.4
$CD_2{=}CD_2$	2.72	.2588	40.4
$CD_2{=}CD_2$	2.72	.2594	40.2
		Av.	40.34 ± 0.2
....	0	1.653	..
....	0	1.628	..
$CH_3CH{=}CH_2$	2.72	1.017	22.6
$CH_3CH{=}CH_2$	2.72	1.010	23.0
$CH_3CH{=}CH_2$	2.72	1.014	22.8
		Av.	22.81 ± 0.2
$CH_3CH{=}CD_2$	2.72	0.970	25.5
$CH_3CH{=}CD_2$	2.72	.969	25.5
		Av.	25.51 ± 0.2
$CD_3CD{=}CD_2$	2.72	.950	26.8
$CD_3CD{=}CD_2$	2.72	.947	27.0
$CD_3CD{=}CD_2$	2.72	.960	26.1
		Av.	26.66 ± 0.3
....	0	.4542	..
....	0	.4554	..
$CH_2{=}CHCH{=}CH_2$	0.0378	.2540	1632
$CH_2{=}CHCH{=}CH_2$	.0378	.2535	1640
$CH_2{=}CHCH{=}CH_2$	.0378	.2538	1635
		Av.	1637 ± 3
$CD_2{=}CDCD{=}CD_2$	.0378	.2321	1981
$CD_2{=}CDCD{=}CD_2$	.0378	.2332	1962
		Av.	1971 ± 8
	Addition of CF_3 radicals		
		$(CF_3H/N_2)^a$	
....	0	0.4615	..
....	0	.457	..
$CH_2{=}CH_2$	0.0735	.349	420
$CH_2{=}CH_2$	.151	.278	427
$CH_2{=}CH_2$	.204	.249	412
$CH_2{=}CH_2$	.259	.219	421
$CH_2{=}CH_2$	.324	.194	420
		Av.	420 ± 6
$CD_2{=}CD_2$	.0735	.344	447
$CD_2{=}CD_2$	.152	.272	452
$CD_2{=}CD_2$	.208	.239	441
$CD_2{=}CD_2$	.263	.208	453
$CD_2{=}CD_2$	.328	.184	455
		Av.	450 ± 6
....	0	.427	..
....	0	.421	..
$CH_3CH{=}CH_2$	.0720	.293	621
$CH_3CH{=}CH_2$	.149	.218	636
$CH_3CH{=}CH_2$	.200	.184	650
		Av.	636 ± 14
$CH_3CH{=}CD_2$	.0723	.285	676
$CH_3CH{=}CD_2$	.149	.210	683
$CH_3CH{=}CD_2$	.200	.178	688
		Av.	683 ± 6
$CD_3CD{=}CD_2$	.0723	.284	686
$CD_3CD{=}CD_2$	.149	.208	699
$CD_3CD{=}CD_2$	.200	.178	688
		Av.	691 ± 7
....	0	.450	..
....	0	.451	..
....	0	.452	..
$CH_2{=}CHCH{=}CH_2$	0.916×10^{-2}	.308	5043
$CH_2{=}CHCH{=}CH_2$	1.89×10^{-2}	.230	5079
$CH_2{=}CHCH{=}CH_2$	2.54×10^{-2}	.202	4860
$CH_2{=}CHCH{=}CH_2$	3.23×10^{-2}	.166	5314
$CH_2{=}CHCH{=}CH_2$	4.04×10^{-2}	.142	5390
		Av.	5137 ± 215
$CD_2{=}CDCD{=}CD_2$	0.96×10^{-2}	.297	5373
$CD_2{=}CDCD{=}CD_2$	1.77×10^{-2}	.215	5583
$CD_2{=}CDCD{=}CD_2$	2.69×10^{-2}	.176	5798
$CD_2{=}CDCD{=}CD_2$	3.41×10^{-2}	.156	5539
$CD_2{=}CDCD{=}CD_2$	4.25×10^{-2}	.130	5783
		Av.	5615 ± 180
....	0	.449	..
....	0	.451	..
....	0	.453	..
$PhCH{=}CH_2$	0.0149	.340	2192
$PhCH{=}CH_2$	.0298	.280	2058
$PhCH{=}CH_2$	.0446	.231	2131
$PhCH{=}CH_2$	.0595	.202	2069
$PhCH{=}CH_2$	.0749	.170	2223
		Av.	2135 ± 75
$PhCD{=}CD_2$	.0132	.342	2451
$PhCD{=}CD_2$	.0262	.281	2325
$PhCD{=}CD_2$	.0392	.236	2319
$PhCD{=}CD_2$	.0524	.203	2334
$PhCD{=}CD_2$	.0655	.180	2301
		Av.	2346 ± 60

[a] (CF_3H/N_2) is given in arbitrary units (ratio of the peaks in the chromatogram).

of CH_3 radicals to α,β,β-trideuteriostyrene and styrene and found its value to be 1.07–1.11. They concluded therefore that the incipient CH_3–C bond is long and the β carbon of styrene retains essentially a planar configuration in the transition state. In the present investigation we extended the work of Matsuoka and Szwarc to other substrates and to additions involving CF_3 radicals as well as CH_3 radicals.

Experimental

The deuteriated compounds investigated were

1. C_2D_4 acquired from Merck, Montreal: mass-spectrographic analysis showed the presence of ~3% C_2D_3H and less than 0.1% of C_2H_4. Gas chromatography showed the absence of chemical impurities.
2. $CH_3CH{=}CD_2$ acquired from Merck, Montreal. The supplier guaranteed the isotopic purity to be more than 98%. Mass spectrographic analysis was inconclusive in determining the per cent of $CH_3CH{=}CDH$ or CH_3-$CH{=}CH_2$. No chemical impurities were found.
3. $CD_3CD{=}CD_2$ acquired from Merck, Montreal: Mass spectrographic analysis showed ~ 4% of C_3D_5H and less than 0.1% C_3H_6. Chemical impurities were absent.
4. $CD_2{=}CDCD{=}CD_2$ acquired from Merck, Montreal. Mass spectrographic analysis showed less than 5% of C_4D_5H. No chemical impurities were detected.
5. $PhCD{=}CD_2$ kindly offered by Dr. Leo Wall of the National Bureau of Standards. The compound was pure chemically and isotopically.

All the gaseous compounds were frozen and thoroughly deaerated before being used for experiments. The hydrogenated compounds were similarly treated. They were all acquired commercially and found to be pure.

Spectroscopic pure grade isoöctane was used as a solvent. This material was passed through a silica column to remove olefinic impurities and moisture.

Azomethane and hexafluoro azomethane were used for generating radicals. The preparation and handling of these compounds are described elsewhere.[9,10] In these last two references are also reported all the details of photolysis, the analysis of products, and the calculation of rate constants. The results are given as the ratio k_2/k_1 where the subscripts refer to the reactions 1 and 2, respectively

$$CH_3 \text{ (or } CF_3) + \text{isoöctane} \longrightarrow CH_4 \text{ (or } CF_3H) + \text{isoöctyl radical} \quad (1)$$

$$CH_3 \text{ (or } CF_3) + \text{substrate} \longrightarrow \cdot\text{substrate}\cdot CH_3 \text{ (or } CF_3) \quad (2)$$

The ratio of the heights of the respective mass spectrographic peaks, determining the masses 16 (CH_4^+) and 28 (N_2^+), was used in determining the relative values of CH_4/N_2 used in calculating the relevant k_2/k_1 values for the CH_3 addition. Similarly, the ratio of the standard gas-chromatogram peaks was used in determining the relative values of CF_3H/N_2, from which the $k_2/k_1(CF_3)$ was calculated. The reliability of these techniques was carefully established (see *e.g.*, ref. 10 and 9).

To assure the best precision of the data, solutions of the hydrogenated and deuteriated compounds were simultaneously photolyzed and then analyzed. The photolysis of two or three "blanks" (solutions not containing the substrate) was performed at the same time. In studying the addition of methyl radicals identical concentrations of the hydrogenated and deuteriated compounds were used, whereas the concentrations of the substrates were varied in studies of CF_3 radical addition. Both methods seem to be satisfactory for determining k_D/k_H.

Results and Discussion

All the experimental results are listed in Table I. The last column of this table gives the values of the ratio of the rate constant of the radical addition (k_2) to the rate constant of H abstraction (k_1). The latter (k_1) is of course constant for the whole series of addition of a particular radical. No attempt was made to determine the temperature coefficient of k_2/k_1, and all the data were obtained at 65°.

It is desirable to notice that the investigated compounds differed greatly in their reactivity. The k_2 values for the CH_3 addition vary by a factor of about 80, and those for the CF_3 addition show a 12-fold variation in their magnitude. As shown in Table II, the variation in the reactivity of the individual substrates is not reflected in the k_D/k_H ratio. The latter were calculated as $\{(k_2/k_1)$ for a deuteriated substrate$/(k_2/k_1)$ for the hydrogenated substrate$\}$. The constancy of k_D/k_H is particularly remarkable in the CF_3 addition.

Several conclusions may be drawn from inspection of Table II. It is obvious that all the k_D/k_H's are only slightly larger than unity and substantially lower than the calculated value of 1.84 expected for the tetrahedral configuration. This, we believe indicates that the incipient R–C bond is relatively long in the transition state and that the remaining groups around the reactive center retain their original planar configuration. This conclusion is supported by the fact that the k_D/k_H seems to be unaffected by the reactivity of the substrate, and that similar values were found for k_D/k_H of the CH_3 and CF_3 radical addition.

Closer examination of the data seems to indicate that k_D/k_H for CF_3 is perhaps slightly lower than k_D/k_H for CH_3 (C_2D_4 being an exception). The difference is very small, and may not be significant, but it might indicate that the incipient CF_3–C bond is longer than the CH_3–C bond. This is a plausible conclusion, since the operation of charge-transfer forces in the reaction of the electrophilic CF_3 radical are expected to reduce the repulsion forces and lengthen the incipient C–CF_3 bond.[3]

The replacement of a hydrogen by deuterium on the carbon atom adjacent to the reactive center seems to be of little importance for the rate of the addition. This carbon atom becomes the seat of an odd electron in the eventually formed adduct radical. The k_D/k_H for $CH_3CH{=}CD_2$ and $CD_3CD{=}CD_2$ are 1.12 and 1.17 for the CH_3 addition and 1.07 and 1.09 for the CF_3 addition. However, we do not think that these small increases are significant, since the k_D/k_H values for $CD_2{=}CD_2$ are 1.05 and 1.07, respectively; *i.e.*, they are not *greater* than those observed for $CH_3CH{=}CD_2$.

TABLE II

SECONDARY DEUTERIUM EFFECT IN CH_3 AND CF_3 ADDITION REACTION

Substrate	k_2/k_1-(CH_3)	$k_2/k_1(CF_3)$	k_D/k_H-(CH_3)	k_D/k_H-(CF_3)
$CD_2{=}CD_2$	40.3	450 ± 6	1.05	1.07
$CH_3CH{=}CD_2$	25.5	682 ± 6	1.12	1.07
$CD_3CD{=}CD_2$	26.6	693 ± 7	1.16	1.09
$PhCD{=}CD_2$	1208	2346 ± 60	1.11[a]	1.10
$CD_2{=}CDCD{=}CD_2$	1971	5615 ± 180	1.20	1.09

[a] This value was taken from ref. 8.

In a recent Note, Wolfsberg and his co-workers[11] criticized Streitwieser's approach to the secondary deuterium effect. They deduced from the general equation of Bigeleisen that the values of k_H/k_D do not determine the configuration of the transition state, *i.e.*, the same k_D/k_H values may be derived whether the transition state be planar or tetrahedral. Wolfsberg's argument is not applicable to our case, although it may be important for the reverse reaction, namely, $\cdot A\cdot CH_3 \rightarrow A + CH_3\cdot$. It could also invalidate a hypothetical conclusion that the transition state is tetrahedral if the k_D/k_H value were found to be high ($\sim$1.8), since then one could argue that the R–C–H bending vibration would be affected even for a planar configuration by the mere vicinity of R. However, the low values of k_D/k_H, found in our studies, are only consistent with the model in which the incipient R–C bond is relatively long and the configuration around the reactive center remains unaltered, *i.e.*, planar.

In a recent Note by Takahasi and Cvetanovic,[12] published after completion of this manuscript, it was shown that k_D/k_H for the addition of H atoms to perdeuteriopropylene and propylene is 1.08 at 25°. This is an additional evidence for the planarity of the transition state.

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