On the other hand, we obtain from (A39)

$$\frac{\partial h(s,0,\theta,\varphi)}{\partial \xi} = \frac{Ca}{\gamma(1/3,\, 30\nu/6D)}\,\frac{3^{2/3}b^{1/3}s^{1/2}}{2^{1/3}D^{1/3}\theta^{1/2}} + C \qquad \text{(A46)}$$

Generally, when Z is very large

$$\gamma(X,Z) \sim \Gamma(X) - Z^{X-1}e^{-Z}\{1 + O(1/Z)\}$$

where $\Gamma\,(X)$ is a gamma function. In our case, $Z = 30\nu/6D = 5 \times 10^{-2}/10^{-5} > 10^3$. Therefore

$$[\Gamma\,(1/3) - \gamma(1/3,Z)] \sim e^{-1000}$$

Accordingly we can put $\gamma(1/3,\, 30\nu/6D) = \Gamma(^1/_3)$. Thus from (A46) we obtain

$$\iint_S \frac{\partial h(s,0,\theta,\varphi)}{\partial \xi}\,\mathrm{d}S = \frac{3^{2/3}b^{1/3}s^{1/2}aC}{2^{1/3}\Gamma(1/3)D^{1/3}}\,2\pi \int_0^{\pi} \frac{\sin\theta}{\sqrt{\theta}}\,\mathrm{d}\theta + 4\pi C$$

$$= \frac{2^{2/3}3^{2/3}(1.79)\pi b^{1/3}s^{1/2}Ca}{\Gamma(1/3)D^{1/3}} + 4\pi C \qquad \text{(A47)}$$

From $c(t,r,\theta,\varphi) = \eta^{-1}f(s,\xi,\theta,\varphi) = (a + \xi)^{-1}f(s,\xi,\theta,\varphi)$ and $f(s,0,\theta,\varphi) = 0$ we can write the relation

$$\left(\frac{\partial c}{\partial r}\right)_{r=R(t)} = \frac{\partial f(s,0,\theta,\varphi)}{\partial \xi}\,\frac{1}{a}\left(\frac{\partial \xi}{\partial \eta}\right)_{\eta=a}\left(\frac{\partial \eta}{\partial r}\right)_{r=R(t)} =$$

$$a^{-1}t^{-1/2}\,\frac{\partial f(s,0,\theta,\varphi)}{\partial \xi} = a^{-1}t^{-1/2}\left\{\frac{\partial g(s,0,\theta,\varphi)}{\partial \xi} + \frac{\partial h(s,0,\theta,\varphi)}{\partial \xi}\right\} \qquad \text{(A48)}$$

From (A45), (A47) and (A48) we obtain the following expression for the concentration gradient in the radial direction at the surface of the mercury drop integrated over the total surface area

$$\iint_S \left(\frac{\partial c}{\partial r}\right)_{r=R(t)} \{R(t)\}^2\mathrm{d}S = C\left\{\frac{4^{1/3}3^{1/6}m^{2/3}t^{1/6}}{\pi^{1/6}d^{2/3}D^{1/2}} + \frac{2^{4/3}3^{1/3}\pi^{2/3}(mt)^{1/3}}{d^{1/3}} + \frac{3^{7/6}(1.79)\pi^{1/2}U^{1/2}(mt)^{1/2}}{\Gamma(1/3)\;30^{1/6}\nu^{1/6}d^{1/2}D^{1/3}}\right\} \qquad \text{(A49)}$$

where $\Gamma\,(^1/_3)$ is equal to 2.680. Using the same numerical constants as for (A23) we obtain the following equation for the average limiting current expressed in terms of amp.

$$i_1 = \frac{1}{t}\int_0^t \left[nFD \iint_S \left(\frac{\partial c}{\partial r}\right)_{r=R(t)} \{R(t)\}^2\,\mathrm{d}S\right]\mathrm{d}t$$

$$= nFCD^{1/2}\{0.238m^{2/3}t^{1/6} + 2.452D^{1/2}(mt)^{1/3} + 0.438U^{1/2}\nu^{-1/6}D^{1/6}(mt)^{1/2}\}$$

The numerical constant of the third term in the brackets corresponds to a parabolic velocity distribution. Converting the unit of current into μa. we obtain equation 18.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK STATE COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY]

Addition of Methyl Radicals to Acetylenic Compounds

BY M. GAZITH AND M. SZWARC

RECEIVED JANUARY 5, 1957

The addition of methyl radicals to several acetylenic compounds was investigated. The activation energies of these addition reactions were found to be higher than those observed in the addition reactions involving the corresponding ethylenic compounds. At the same time it was observed that the entropies of activation are also higher in the additions to the acetylenic compounds. The following pair of compounds were compared: acetylene–ethylene, methylacetylene–propylene, dimethylacetylene–the butenes-2, phenylacetylene–styrene, and diphenylacetylene–the stilbenes. It is suggested that the difference in the reactivity of a C≡C triple bond as compared with a C=C double bond arises from two factors. The π electrons in the shorter C≡C bond interact more strongly and consequently higher activation energy is necessary for the addition process which utilizes one of these electrons. On the other hand, the cylindrical symmetry of the C≡C bond leads to higher entropy of activation than the planar symmetry of the C=C double bond.

During the last few years a considerable amount of work has been carried out in these laboratories on the addition of radicals to aromatic and olefinic compounds.[1-6] The reactions investigated are represented by the general equation

$$\mathrm{R + A \longrightarrow R.A}$$

where R denotes a radical, A represents a molecule of an aromatic or an olefinic compound, and R.A represents the primary addition product which, of course, is also a radical. Most of these investigations dealt with the addition of methyl radicals, and the relative rate constants of such additions, denoted as methyl affinities, were measured by the ratios k_2/k_1, where the subscripts refer to the two reactions[7]

$$\mathrm{CH_3 + solvent \longrightarrow CH_4 + solvent\ radical} \qquad (1)$$

$$\mathrm{CH_3 + A \longrightarrow A.CH_3} \qquad (2)$$

The investigation reported in the present communication deals with the addition of methyl radicals to acetylenic compounds. The main purpose of this study was to find how the reactivity of a C≡C triple bond differs from that of a C=C double bond, and to interpret this difference in terms of electronic structures of the respective compounds.

Experimental

The following acetylenic compounds were investigated: acetylene, methylacetylene, dimethylacetylene, phenylacetylene, diphenylacetylene, and dimethyl ester of acetylene dicarboxylic acid. Acetylene was purchased from Matheson Co. and was 99.5% pure. The gas was deaerated and then distilled from trap to trap, the middle portion being collected. In some experiments the gas used was twice distilled. This additional purification did not affect the results indicating that our rate constants for acetylene are genuine.

High purity grade methylacetylene and dimethylacetylene were obtained from Farchan Research Laboratories. These compounds were used without further purification. Phenylacetylene and diphenylacetylene were prepared and purified by Dr. Bader from Aldrich Chemicals.[8] Finally, the dimethyl ester of acetylene dicarboxylic acid was prepared in our laboratories from the respective dicarboxylic acid. The ester was purified by fractionation *in vacuo*.

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[1] M. Levy and M. Szwarc, THIS JOURNAL, **77**, 1949 (1955).

[2] M. Szwarc, *J. Polymer Sci.*, **16**, 89 (1955).

[3] A. Rembaum and M. Szwarc, THIS JOURNAL, **77**, 4468 (1955).

[4] F. Leavitt, M. Levy, M. Szwarc and V. Stannett, *ibid.*, **77**, 5493 (1955).

[5] R. P. Buckley and M. Szwarc, *ibid.*, **78**, 5696 (1956).

[6] J. Smid and M. Szwarc, *ibid.*, **78**, 3322 (1956).

[7] The same solvent was used in each series of investigated compounds A's. Hence, k_1 remains constant throughout the series.

[8] We take this opportunity to thank Dr. Bader for his assistance.

Acetyl peroxide was prepared by the method described previously[9]; the compound was twice crystallized in an apparatus described by Mundy[10] and then dissolved in spectroscopically pure isoöctane. We used in our work 5×10^{-3} *M* and 5×10^{-3} *M* solutions of acetyl peroxide.

Experiments were carried out at four temperatures, namely, 55, 65, 75 and 85°. The experimental procedure and the method of analysis were described previously[1,11] and need not be repeated again. However, some modifications were introduced in the work involving gaseous compounds. For these compounds we used a reaction vessel shown in Fig. 1. The solution of acetyl peroxide in isoöctane was introduced into the spherical container, deaerated by the repeated freezing and thawing technique. Thereafter, the desirable amount of the gaseous compound was condensed in it by cooling the flask with liquid nitrogen. The stopcock leading to the vacuum line was then closed, and by turning the reaction flask round the ground joint No. 2, all the contents were transferred into ampoule A cooled now by liquid nitrogen.[12] Finally the ampoule was sealed off at constriction C, heated for a desired time at the required temperature, and then quickly cooled by immersion in a solid carbon dioxide-acetone bath. Eventually the ampoule was placed in a special device in which the tip of the ampoule could be broken *in vacuo*. Then the contents of the ampoule were analyzed in the usual way.

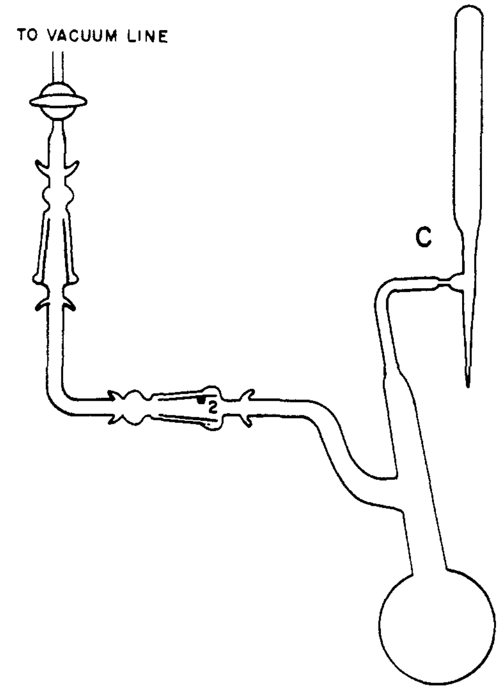

Fig. 1.

Results and their Evaluation

It was shown previously[1,2] that the ratio of the rate constants k_2/k_1 can be evaluated from the equation

$$k_2/k_1 = \{[A^0(\mathrm{CH_4}) - A(\mathrm{CH_4})]/A(\mathrm{CH_4})\}(X_{\mathrm{HS}}/X_{\mathrm{A}})$$

In this equation $A^0(\mathrm{CH_4})$ and $A(\mathrm{CH_4})$ denote the amounts of methane formed in two experiments carried out under identical conditions except that in one the olefinic or aromatic compound was present, while in the other was absent. The symbols X_{HS} and X_{A} denote the mole fractions of the solvent and the investigated olefinic or aromatic compound.

It was considered[4] that the substitution of $A^0(\mathrm{CH_4})$ and $A(\mathrm{CH_4})$ by $A^0(\mathrm{CH_4})/(\mathrm{CO_2})$ and $A(\mathrm{CH_4})/(\mathrm{CO_2})$ might be advantageous. While the former entities are dependent on the time of experiment, on the amount of the peroxide used, and are very sensitive to small changes in the temperature, the latter are independent of the amount of the peroxide used and the time of experiment, and only slightly affected by the temperature. The experimental advantage is therefore obvious.

On the other hand, the determination of $A^0(\mathrm{CH_4})$ and $A(\mathrm{CH_4})$ requires one measurement for each, while the ratios $A^0(\mathrm{CH_4})/(\mathrm{CO_2})$ and $A(\mathrm{CH_4})/(\mathrm{CO_2})$ are derived from two measurements for each ratio. Hence, the experimental errors are squared in the latter method and this drawback might outweight the advantages mentioned previously. In this investigation both methods were used in determining the k_2/k_1 ratios for phenylacetylene and diphenylacetylene in order to find which of these is more reliable. The results are given in Table I and they show that both methods lead to values which essentially are identical within their respective experimental errors. The only considerable deviation was observed in experiments involving diphenylacetylene and carried out at 85°. We believe that the value based on the $A(\mathrm{CH_4})/(\mathrm{CO_2})$ ratio obtained in this particular series of experiments is less reliable and it appears to be too high. It is also worth noticing that the scatter of the results appears to be nearly the same in both methods, indicating that both are equally reliable.

The reliability of these two methods was tested further by plotting the $\log(k_2/k_1)$ against the reciprocal of absolute temperature, as shown in Fig. 2.

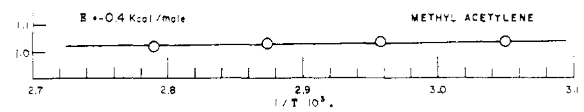

Fig. 2.

The differences in activation energies and A_2/A_1 factors calculated for the reaction involving phenylacetylene were well within the experimental errors (see Table III). However, the agreement does not seem as good for diphenylacetylene, apparently because of the high value of k_2/k_1 determined at 85° by the $A(\mathrm{CH_4})/(\mathrm{CO_2})$ method. We mentioned earlier that this determination seems to be inaccurate and if this result is discarded the respective *E* and A_2/A_1 values agree reasonably with those obtained by the alternative method.

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[9] M. Levy and M. Szwarc, This Journal, **76**, 5978 (1954).

[10] Mundy, Ph.D. Thesis, 1951, Cornell University.

[11] M. Levy and M. Szwarc, This Journal, **76**, 5981 (1954)

[12] The amount of solution used was chosen in such a way that the ampoule A was nearly full, thus the error caused by the volatility of the gaseous olefins was minimized.

TABLE I

Temp., °C.	Mole %	CH_4,[a] mm. Hg	CH_4/CO_2[b]	k_2/k_1, based on CH_4	k_2/k_1, based on CH_4/CO_2
		Phenylacetylene			
54.7	...	0.266	0.805	...	...
	0.260	.183	.515	174	216
	0.519	.135	.373	187	222
	1.04	.090	.281	188	174
	2.07	.056	.159	179	192
			Av.	182 ± 7	201 ± 22
64.9	...	0.199	0.805	...	...
	0.260	.139	.514	166	217
	.579	.105	.417	195	178
	.778	.086	.330	166	184
	1.04	.071	.267	173	193
	1.04	.067	.252	187	210
	2.07	.044	.161	167	189
			Av.	177 ± 12	195 ± 15
74.8	...	0.242	0.805	...	...
	0.260	.169	.550	166	178
	.519	.128	.424	170	172
	1.04	.085	.282	177	177
	2.07	.049	.167	185	180
			Av.	174 ± 8	177 ± 4
85.2	...	0.187	0.805	...	...
	0.260	.130	.561	168	167
	.519	.104	.435	154	163
	1.04	.071	.289	156	170
	1.04	.071	.297	156	164
	2.07	.045	.186	149	158
			Av.	157 ± 7	164 ± 5
		Diphenylacetylene			
54.7	..	0.266	0.805	...	...
	1.02	.222	.682	(19.3)	(17.6)
	2.01	.202	.633	15.5	13.2
	4.01	.163	.518	15.1	13.3
	8.70	.123	.379	12.3	11.8
			Av.	13.7 ± 1.6	12.4 ± 0.9
64.9	..	0.199	0.805	...	...
	1.02	.174	.686	(14.0)	(16.9)
	2.01	.159	.644	12.3	12.2
	4.01	.125	.539	14.3	11.8
	8.70	.095	.375	11.5	12.1
			Av.	12.7 ± 1.2	12.0 ± 0.2
74.8	..	0.242	0.805	...	...
	1.02	.215	.713	12.2	12.6
	2.01	.185	...	(15.1)	...
	4.01	.152	.493	14.2	15.2
	8.70	.113	.381	12.0	11.7
			Av.	12.8 ± 1.5	13.2 ± 1.5
85.2	..	0.187	0.805	...	...
	1.02	.170	.684	(9.75)	(17.3)
	2.01	.152	.612	11.1	15.4
	4.01	.121	.471	13.1	16.4
	8.70	.089	.363	11.6	12.8
			Av.	11.9 ± 0.9	14.9 ± 1.5

[a] The amount of CH_4 formed in absence of acetylenes is the average of a few experiments carried out simultaneously with various runs. Such experiments were carried out at each of the temperatures used in this investigation. [b] The ratio CH_4/CO_2 is the average of *all* the experiments carried out at temperatures 55–85°. It appears that this ratio is temperature independent within the investigated range of temperature.

Discussion

Inspection of Tables I and II shows that the values of k_2/k_1 calculated for acetylene, methylacetylene, phenylacetylene and diphenylacetylene are constants independent of the concentration of the acetylenic compound. This means that the abstraction of hydrogen atoms by methyl radicals from these compounds is negligible as compared to the methyl radical addition reaction, a conclusion particularly significant for methylacetylene.

TABLE II

Compound	T, °C.	Range of concn., %	No. expt.	k_2/k_1
Acetylene	54.7	2.8–6.6	6	30.1 ± 1.63
	64.9	2.8–7.6	5	29.4 ± 3.26
	74.8	3.0–7.8	4	28.4 ± 0.70
	85.2	3.0–6.5	4	30.1 ± 1.66
Methylacetylene	54.7	4.8–11.6	4	11.05 ± 1.69
	64.9	4.2–12.0	4	10.85 ± 0.95
	74.8	4.9–11.7	3	10.86 ± 0.69
	85.2	5.2–11.5	3	10.39 ± 0.70
				$(k_2k_1)_{exp}$
Dimethylacetylene	54.7	5.6–19.1	3	1.26–0.44
Extrapolated to 0%; k_2/k_1 = 4.7				
	64.9	7.8–22.0	3	0.8–0.4
Extrapolated to 0%; k_2/k_1 = 1.4				
	74.8	9.2–20.9	3	1.16–0.21
Extrapolated to 0%; k_2/k_1 = 2.0				

On the other hand, the same calculations applied to the results obtained for dimethylacetylene lead to a variable entity, denoted in Table II as $(k_2/k_1)_{exp}$ which decreases with the increasing mole fraction of the compound. It was shown elsewhere[13] that such a result is due to the abstraction of hydrogen atoms from the investigated compound by methyl radicals, and that the ratio k_2/k_1 is then obtained by plotting the reciprocal of $(k_2/k_1)_{exp}$ *versus* the mole fraction of the investigated compound. Such a plot results in a straight line, intercept of which gives the reciprocal of the k_2/k_1. Using this method we computed the respective k_2/k_1 listed in Table II. However the experimental data lead to considerable uncertainties and therefore the quoted values represent only the magnitude of the respective rate constants.

It is interesting to compare the addition of radicals to C≡C triple bonds and to the corresponding C=C double bonds. The addition of a radical leads eventually to the formation of a new C–C σ bond, and this process utilizes one of the π electrons of the multiple bond. Hence, whenever the interaction of the π electrons is stronger, *i.e.*, whenever the exchange integral β is more negative, the activation energy of the addition reaction should be larger. Since C≡C triple bonds are shorter than the C=C double bonds, the interaction between their π electrons is more powerful. Therefore, the activation energy of the addition reaction involving a C≡C bond should be larger than the activation energy of the reaction involving a corresponding C=C double bond, if our argument is correct. This conclusion seems to be confirmed by the data listed in Table III. All the activation energies quoted in this

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[13] R. P. Buckley, F. Leavitt and M. Szwarc, THIS JOURNAL, **78**, 5557 (1956).

TABLE III

Acetylenic compd.	k_2/k_1 at 65°	$E_2 - E_1$, kcal./mole	A_2/A_1	Olefinic compd.	k_2/k_1 at 65°	$E_2 - E_1$, kcal./mole	A_2/A_1
Acetylene	29.4	0.0	30	Ethylene[a]	34.0	−0.6	13.0
Methylacetylene	10.8	−0.4	5.0	Propylene[a]	22	−1.1	4.3
Dimethylacetylene	~2	...	..	Butene-2[a]			
				trans	6.9	−1.9	0.4
				cis	3.4	−1.9	0.2
Phenylacetylene				Styrene[b]			
(CH_4)	177	−1.1	32		792	−3.0	9.0
(CH_4/CO_2)	195	−1.8	95				
Diphenylacetylene				Stilbene[b]			
(CH_4)	12.7	−1.0	3.4	*trans*	104	−2.4	3.1
(CH_4/CO_2)	12.0	+1.5 (?) or +0.7[c]	80 (?) or 37[c]	*cis*	29	−1.0	5

[a] R. P. Buckley, A. Rembaum and M. Szwarc, *J. Polymer Sci.*, 24, 135 (1957). [b] F. Leavitt, M. Levy, M. Szwarc and V. Stannett, THIS JOURNAL, 77, 5493 (1955). [c] These values were obtained by discarding the results obtained at 85°.

table were calculated by the least square method. Although the differences which interest us are small, and in some cases their magnitude is comparable to the experimental errors, the consistency of the observed trends supports our suggestion that in the addition reaction a C≡C triple bond acts as a "compressed" C=C double bond.[14]

The cylindrical symmetry of a C≡C bond as compared to the planar symmetry of a C=C double bond implies that the A factors (*i.e.*, entropy of activation) should be greater for the addition of radicals to the acetylenic compounds. This conclusion seems also to be substantiated by the data listed in Table III.

Since the nature of the C≡C bond affects in the same direction the activation energy and the *A* factor, one cannot predict how the rate of addition to the C≡C bond would compare with the rate of addition to the C=C double bond. For example, the rate of addition of methyl radicals to acetylene is comparable with the rate of addition to ethylene; on the other hand, the rates of addition to the other investigated acetylenic compounds are lower than those observed for the respective olefinic compounds.

Finally, let us compare the rate of addition of methyl radicals to acetylenic compounds with those of addition of other radicals. The only quantitative data available came from the studies of copolymerization processes. Thus, Doak[15] investigated the copolymerization of methyl acrylate and acrylonitrile with phenylacetylene, diphenylacetylene and hexyne. From his data one derives the values listed in Table IV for the relative rate constants of the addition of methyl acrylate radicals and acrylonitrile radicals to the acetylenic compounds. The results show some similarities for all the three radicals investigated. The steric hindrance is probably responsible for lower reactivity of diphenylacetylene as compared with phenylacetylene, and the smallest effect is observed in the attack by the smallest radical, *i.e.*, methyl radical. On the other hand, the lower reactivity of hexyne (or propyne) as compared with phenylacetylene reflects the higher resonance stabilization of the radical formed from the latter molecule and therefore the effect is shown for each of the three radicals listed in Table IV.

TABLE IV

	Methyl acrylate radical		Acrylonitrile radical		Methyl radical at 65°
Acetylenic compd.	$1/r_1$ at 60°	Relative value of the addition constant	$1/r_1$ at 60°	Relative value of the addition constant	relative value of the addition constant
Phenylacetylene	1.6	(1.0)	3.85	(1.0)	(1.0)
Diphenylacetylene	0.018	0.011	0.074	0.019	0.071
Hexyne (or propyne)	0.09	0.056	0.018	0.0047	0.06

The data listed in Table IV can be compared in a different way, namely, by computing the ratio of the rates of addition of radicals to phenylacetylene and to styrene. The following results are obtained

	Methyl acrylate radical	Acrylonitrile radical	Methyl radical
$\frac{k \text{ for addition to styrene}}{k \text{ for addition to phenylacetylene}}$	~6	3.5	4.5

The higher reactivity of styrene as compared with phenylacetylene was discussed by Doak in terms of higher resonance energy of the radical Ph.CH.CH$_2$.X as compared with Ph.Ç = CH.X. We believe, however, that our explanation is more correct, namely, the uncoupling of a π electron is more difficult in a short C≡C bond than in the longer C=C bond.

The fact that the ratios of the rate constants of addition to styrene and to phenylacetylene is approximately the same for three radicals of different polarities seems to indicate that the polarities of both styrene and phenylacetylene are close to zero.

After completion of this work, Mr. Buckley, working in our laboratories, investigated the addition of methyl radicals to pentyne-1 and hexyne-1. These results are summarized in Tables V and VI and Fig. 3. They lead to the following conclusions. Methyl radicals react with pentyne-1 and hexyne-1 in a dual fashion: add to the triple C≡C bond or abstract α hydrogen atom from the CH_2 group adjacent to the C≡C bond. The relevant rate constants are calculated from the plots of $(k_2/k_1)^{-1}_{\text{exp}}$ *versus* x_a/x_s (for the details of the method see ref. 10) by the least square method. These calculations show that k_2/k_1 for pentyne-1 and hexyne-1 at 65° are 13.7 and 17.5, respectively. Both these values

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(14) See in this connection a paper by F. Leavitt and M. Szwarc, THIS JOURNAL, 78, 3590 (1956), in which the reactivity of a stretched C=C double bond is discussed.

(15) K. W. Doak, *ibid.*, 72, 4681 (1950).

TABLE V

T = 65°C., SOLVENT ISOÖCTANE

Hydrocarbon	Mole, %	$(k_2/k_1)_{exp.}$
Pentyne-1	10.51	4.61
Pentyne-1	7.88	5.94
Pentyne-1	5.26	7.30
Pentyne-1	2.63	9.26
Pentyne-1; k_2/k_1 extrapolated to 0 mole % = 13.7		
Hexyne-1	10.45	6.00
Hexyne-1	7.84	7.00
Hexyne-1	5.24	8.86
Hexyne-1	2.62	12.50
Hexyne-1; k_2/k_1 extrapolated to 0 mole % = 17.5		

TABLE VI

T = 65°C., SOLVENT ISOÖCTANE

Hydrocarbon	k_2/k_1	k_5/k_2	k_5/k_1	k_5'/k_1
Pentyne-1	13.7	1.2	16.3	8.1
Hexyne-1	17.5	0.97	17.0	8.5

compare reasonably with the k_2/k_1 value determined for methylacetylene, namely, 10.85, and thus it appears that the rate of addition of methyl radicals to an acetylene of the type CH≡C—R is, at least approximately, independent of the length of the group R.

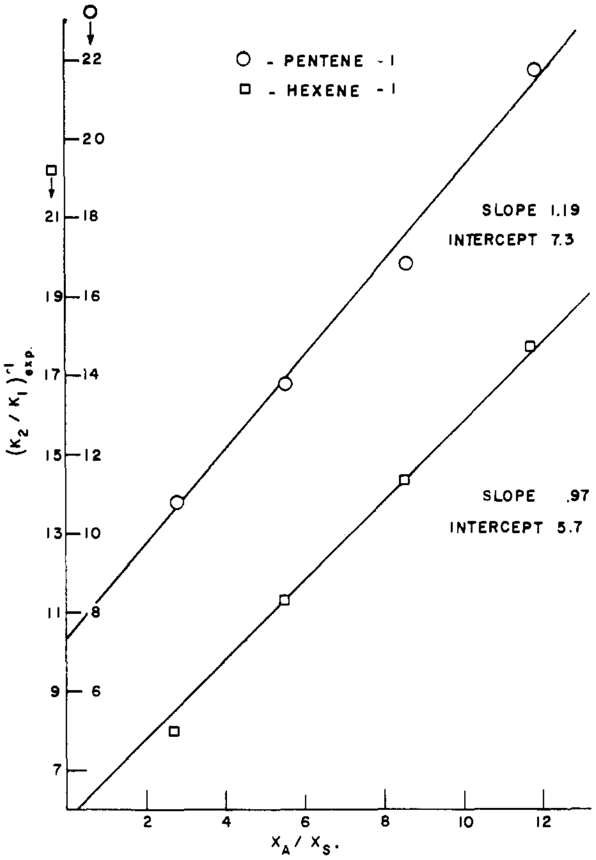

Fig. 3.

It is interesting to compare the rate of abstraction of hydrogen atoms from the CH_2 group α to C≡C triple bond with the rate of abstraction from the same group α to C=C double bond. The results arrived at from the study of reactions of pentyne and hexyne lead to values 8.1 and 8.5, respectively, for the ratio k_5'/k_1 (k_5' represents the rate constant of hydrogen abstraction reaction per active hydrogen, *i.e.*, $k_5/2$ for the discussed hydrocarbons). On the other hand, the work of Buckley and Szwarc[12] demonstrated that the corresponding values of k_5'/k_1 for butene-1, pentene-1, heptene-1, decene-1 and hexadecene-1 are 3.3, 4.1, 6.3, 6.4 and 6.4, respectively. It appears, therefore, that the rate of abstraction of a hydrogen atom from a CH_2 group adjacent to a C≡C triple bond is slightly higher than the corresponding rate for a reaction involving a CH_2 group adjacent to a C=C double bond. This point will be discussed further in a forthcoming publication.

In conclusion we wish to thank the National Science Foundation for their support of this investigation.

SYRACUSE, N. Y.

[CONTRIBUTION FROM BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Photochemical Exchange of Water between $Cr(H_2O)_6^{+3}$ and Solvent[1]

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Studies have been made on the rate of the reaction $Cr(H_2O)_6^{+3} + 6H_2O^{18} \rightarrow Cr(H_2O^{18})_6^{+3} + 6H_2O$ in the presence of light of various wave lengths. Quantum yields have been obtained for the three $Cr(H_2O)_6^{+3}$ absorption bands (2610, 4080, 5740 Å.) at three temperatures (0, 10, 27°). At 27°, the quantum yields for all bands are of the order of magnitude 10^{-2}, and decrease with decreasing temperature. Solutions of $Cr(H_2O)_6(ClO_4)_3$ were carefully checked for fluorescence which was found to be absent even at −196° in glasses prepared by dissolving $Cr(H_2O)_6(ClO_4)_3$ in isopropyl alcohol. In order to account for the low quantum yields and absence of fluorescence, it seems most likely that the electronically excited chromic species converts to the ground state by radiationless transitions to high vibrational states of the ground electronic level. Because of the large temperature dependence of the photochemical reaction, it appears more probable that reaction occurs from an excited electronic state rather than from an excited vibrational state. However, such an interpretation seems to demand that during deactivation, some of the chromic species must pass through a spin forbidden (doublet) state.

For many years it has been known that some substitution reactions of complex ions are hastened by light. Most such reactions seem to be particularly sensitive to ultraviolet radiation, and the mechanisms which have been proposed usually involve an electron transfer followed by rapid substitution. For example, for a series of complex ions of the type $[Co(NH_3)_5X]^{++}$ (in which X is F^-, Cl^-, Br^- or I^-)

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