of our conclusion that dioxane is not an effective complexing agent for malonic acid in the sense defined above. To test this assumption suppose that K_{1D} is so much smaller than K_{1Q} as to be effectively zero, and that although $(K_1/2K_3)_D = (K_4/K_3)_D$, they are different from unity. Then, using model II for computation (the test is most stringent with this model), we have

$$L(k_1/2k_3)_{\text{obsd Q}} - L(k_1/2k_3)_{\text{obsd D}} = L(P_Q) - L(P_D) = 0.80 \pm 0.13$$

Substitution of the value of K_{1Q} into the ratio P_Q/P_D yields $(K_1/2K_3)_D = 0.81525\,(K_1/2K_3)_Q + 0.17684$. Consider three values for $(K_1/2K_3)_Q$ related to the discussion above: 1.0200, 1.0097 and 0.9800; the corresponding values of $(K_1/2K_3)_D$ are 1.0084, 1.0000 and 0.9758. The largest possible value for $(K_1/2K_3)_D$ is 1.0084, when the corresponding quantity for quinoline is at the assumed 2% effect upper limit; the minimum value, 0.98, corresponds to $(K_1/2K_3)_Q = 0.9852$, *the larger relative equilibrium isotope effect being associated with the weaker complexing agent.* In view of the great disparity between K_{1Q} and K_{1D} this situation is unreasonable. The value estimated for K_{1Q} is a maximum, so 1.0097 represents a probable maximum for $(K_1/2K_3)_Q$; since, if they both differ from unity, the sense with respect to unity of $(K_1/2K_3)_Q$ and $(K_1/2K_3)_D$ should be the same, the assumption that the latter is indistinguishably different from unity is warranted. A more definite test of this point could be made if values of P_Q'/P_D' were available.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

Some Reactions of the Allyl Radical

BY ALVIN S. GORDON, S. RUVEN SMITH AND JAMES R. MCNESBY[1]

RECEIVED JULY 7, 1958

In a previous publication[2] it was shown that allyl radicals disappear *via* radical–radical reactions until about 450°. At this temperature allyl radicals abstract hydrogen sufficiently well so that propylene appears in the products early in the reaction. With increasing temperature, hydrogen is abstracted more readily until, at temperatures over 500°, it is a more important reaction than disappearance *via* radical–radical processes. In the present paper it is shown that the energy of activation for abstraction of hydrogen from cyclopentane by allyl radicals is 31.8 ± 3.6 kcal. (std. deviation). The corresponding value for abstraction by methyl radicals is 9.3 kcal. In addition, the allyl radical and the methyl radical are shown to discriminate between H and D abstraction in about the same way.

Introduction

There are no reported data in the literature for abstraction of H atoms by allyl radicals over a temperature range. Szwarc[3] and his colleagues have estimated a value of 14–17 kcal. for abstraction of H from toluene by the allyl radical.

The value of the activation energy for the abstraction of H from the cyclopentane is of interest because of the large resonance energy in the allyl radical. It is also of interest to establish the energy of activation difference for abstraction of H and D atoms compared to the same difference for the methyl radical.

Experimental

Apparatus and Materials.—A cylindrical quartz reaction flask with flat parallel windows was placed in an aluminum block furnace. It was irradiated by an SC-100 medium pressure mercury lamp.[4] The lamp was housed in a parabolic mirror housing, set co-axially with the axis of the reaction vessel.

Approximately equimolar mixtures of cyclopentane and acetone-d_6[5] (Ad_6) were used. A chromatogram of the mix showed it to be free of impurities. They were photolyzed with the full beam of the SC-100 lamp and the products toeplered into a flask with two break seals. The reaction was allowed to proceed less than 2% toward completion. The small side arm through which the gases were admitted was sealed off from the system by black Apiezon wax to avoid pyrolyzing any constituents. Finally the side tube was sealed off above the Apiezon wax. The sample flask was attached to a gas chromatography unit and the seals broken after the volume above the break seal was thoroughly evacuated. The contents of the flask were swept onto the column by helium. We used a technique previously described[6] of reproducibly increasing the temperature of the column during the run. A 6-ft. 1.5 wt. % squalane on Pelletex[7] column was used with a starting temperature of −190°. The methane and propylene fractions were trapped and analyzed on the mass spectrometer. The areas of the methane, propylene and butene-1 fractions were measured by an electronic integrator.

Results and Discussion

Methane, propylene and butene-1 formations are controlled by the reactions

$$CD_3COCD_3 \xrightarrow{h\nu} 2CD_3 + CO \qquad (1)$$

$$CD_3 + \square \longrightarrow CD_3H + \square\cdot \qquad (2)$$

$$CD_3 + Ad_6 \longrightarrow CD_4 + CD_2COCD_3 \qquad (2a)$$

$$\square\cdot \longrightarrow C_2H_4 + CH_2CH{=}CH_2 \qquad (3)$$

(1) National Bureau of Standards, Washington, D. C.

(2) J. R. McNesby and A. S. Gordon, THIS JOURNAL, **79**, 825 (1957).

(3) M. Szwarc, B. N. Ghosh and A. H. Sehon, *J. Chem. Phys.*, **18**, 1142 (1950).

(4) Manufactured by Hanovia.

(5) Manufactured by Merck Ltd., Montreal, Canada.

(6) C. M. Drew, J. R. McNesby, S. R. Smith and A. S. Gordon, *Anal. Chem.*, **28**, 979 (1956).

(7) Special carbon black manufactured by G. Cabot.

TABLE I

No.	°K.	Time (sec.)	Total methane[a]	CD_3H methane[a]	Total propylene[a]	$CH_3CH{=}CH_2$ propylene	Butene-1-d_3	$\left(\square\right)^2$ mm.[b] 10^{-2}	log A[c]
621	722.5	420	1394	1210	183	161	232	109.35	0.2617
622	733	420	1232	1066	247	217	206	95.35	.4478
623	733	420	1227	1062	277	244	209	99.24	.4735
624	743.5	420	1098	947	208	183	159	83.5	.4922
625	751.5	360	1119	963	354	310	217	92.56	.6158
627	769.5	300	970	831	514	449	155	87.40	.9633
628	785.0	180	600	512	499	435	65	86.53	1.3414
6201	743.7	420	1141	984	263	231	174	80.87	0.5851
6203	724.3	450	1265	1098	229	202	256	91.83	.3214
6204	734.0	420	1153	997	122	107	122	97.02	.3318
6207	768	450	883	756	345	217	126	30.85	.9727
6209	778	300	513	439	241	210	112	25.18	1.0374
632	758.5	310	1539	1323	437	382	194	85.49	0.9927
633	725	450	1840	1596	241	212	236	99.44	.5058
634	735	420	1863	1611	288	253	225	104.65	.6151
639	732.5	420	1452	1257	127	112	197	57.02	.4749
6313	767.5	250	1073	919	289	253	174	47.29	1.0542
6314	756.5	240	1042	896	526	461	188	62.92	1.1629
617	753	390	1074	929	316	276	186	68.18	0.7143
618	787	300	1065	907	918	799	167	62.41	1.3644

[a] All these values are arbitrary area units from the gas chromatogram.
[b] These are relative values.
[c] $A = \dfrac{(CD_3H)(CH_3CH{=}CH_2)}{(CD_3CH_2CH{=}CH_2)(t)\left(\square\ \text{rel}\right)^2} \times 10^{-2}$.

$$CH_2CH{=}CH_2 + \square \longrightarrow CH_3CH{=}CH_2 + \square \cdot \quad (4)$$

$$CH_2CH{=}CH_2 + Ad_6 \longrightarrow CH_2DCH{=}CH_2 + CD_2COCD_3 \quad (4a)$$

$$CD_3 + CH_2CH{=}CH_2 \longrightarrow CD_3CH_2CH{=}CH_2 \quad (5)$$

Reaction 3 has been shown to occur at temperatures above 250°.[7] Reaction 4 is important above 450°, its importance increasing with temperature. The species CD_4 and $CH_2DCH{=}CH_2$ also occur from the abstraction of a D from acetone-d_6 by CD_3 and allyl radicals, respectively. Some d_0-, d_1-, d_2- and d_3-propylene is produced *via* the reaction of CD_3 with ethylene.[8] Fortunately, these appear in minor amounts since no propylene appears in the chromatogram at temperatures of 300–400° where propylene formation from methyl and ethylene has been shown to be more efficient than at the higher temperatures of our experiments. Ethylene is present from 250° upward due to reaction 3.

The partial pressure of acetone and the optical path through the reaction vessel is small, and we assume that the steady-state concentration of radicals is uniform throughout the reaction vessel. Also, less than 2% of our reaction mixture reacts so that the concentration of reactants may be taken as constant. Under these conditions

$$\frac{d(CD_3H)}{dt} = k_2(CD_3)\left(\square\right) \quad (I)$$

$$(CD_3H) = k_2(CD_3)\left(\square\right)(t) \quad (II)$$

where t = time of photolysis in seconds. Equation II follows from I since only the early part of the reaction is studied and $\left(\square\right)$ remains sensibly constant during this time. Similarly

$$(CH_3CH{=}CH_2) = k_4(CH_2CH{=}CH_2)\left(\square\right)(t) \quad (III)$$

$$(CD_3CH_2CH{=}CH_2) = k_5(CD_3)(CH_2CH{=}CH_2)(t) \quad (IV)$$

$$\frac{(CD_3H)(CH_3CH{=}CH_2)}{(CD_3CH_2CH{=}CH_2)} = k_2\frac{(CD_3)\left(\square\right)(t)k_4(CH_2CH{=}CH_2)\left(\square\right)(t)}{k_5(CD_3)(CH_2CH{=}CH_2)(t)} \quad (V)$$

$$\frac{k_2k_4}{k_5} = \frac{(CD_3H)(CH_3CH{=}CH_2)}{(CD_3CH_2CH{=}CH_2)\left(\square\right)^2(t)} \quad (VI)$$

We make the following assumptions:

1. The amount of propylene and butene-1 is proportional to the area of the compound on the chromatogram peak over the ranges studied in this work. It should be noted that this does not imply that the proportionality constant is the same for different compounds. It has been demonstrated previously in these laboratories that the proportionality constant holds over a very wide range for methane.

2. The energy of activation for reaction 5 is zero.

The total methane and propylene peaks are corrected to the CD_3H and $CH_3CH{=}CH_2$ contributions by the CD_3H/CD_4 and $CH_3CH{=}CH_2/CH_2CDH{=}CH_2$ ratios.[9] Because of a trace of d_3- and d_2-propylene in the samples, the propylene ratios are not as precise as the methane ratios. Since the light propylene is about 85% of the total, the inaccuracies in the above ratio do not seriously affect the results. The logs of the right-hand side

(8) A. S. Gordon and J. R. McNesby (private communication).

(9) $CH_2DCH{=}CH_2$ was kindly prepared for us by Dr. William Norris of the Chemistry Division, U. S. NOTS. The prepared sample was purified on a gas chromatographic column, and the propylene fraction was trapped and used as a mass spectrometer standard.

of equation VI are shown in Table I, along with the corresponding temperatures. When these values are fitted in an Arrhenius plot, the slope is $E_0/2.3R$ where $E_0 = E_2 + E_4 - E_5$.

The least squares fit for the slope gives a value of $E_0 = 41.1 \pm 3.6$ kcal. (std. deviation). We have shown[10] previously that $E_2 = 9.3$ kcal., and it follows that $E_4 = 31.8 \pm 3.6$ kcal. (std. deviation), assuming $E_5 = 0$. The value of 9.3 is within a tenth of a kcal. of the value previously obtained by us for the abstraction of the secondary H in butane.[11] There is probably little or no strain in the ring. The strength of the C–H bond in cyclopentane is thus about 94 kcal. Sehon and Szwarc[11] have obtained a value of 77 kcal. for the $H-CH_2CHCH_2$ bond. The minimum activation energy for abstraction of H from cyclopentane by the allyl radical is thus 17 kcal. However, it should be remembered that the abstraction reactions of methyl radicals, which are all exothermic, proceed with activation energies of about 10 kcal., so that for the allyl radical the energy can reasonably be expected to be somewhat greater than 17 kcal.

The value for the difference in E_{act} for abstraction of D from acetone-d_6 and H from cyclopentane by allyl radical and by methyl radical may be obtained from an Arrhenius plot of the $CH_3CH{=}CH_2/CH_2DCH{=}CH_2$ and CD_3H/CD_4 ratios, respectively. The values are 1.9 ± 0.52 kcal. (std. deviation) for the allyl radical and 2.4 ± 0.23 kcal. for the methyl radical. The two values are the same within experimental error, showing that the discrimination barrier is the same for both radicals. It should be noted that our present value for the E_{act} difference for methyl radical abstraction is within 0.3 kcal. of the value we reported for the same system at a somewhat lower temperature.[10] The standard deviation shows that our present values are not as precise as the previous values.

Pyrolysis of Mixtures of Cyclopentane and Ad_6.—Mixtures of Ad_6 and cyclopentane were pyrolyzed in quartz and Pyrex vessels and packed in Pyrex vessels with glass wool which increased the surface/volume by a factor of 100 over the unpacked vessels. In the temperature range of 500° the rate of pyrolysis is about the same in quartz and in Pyrex vessels of the same dimensions. The hundredfold increase in s/v increased the pyrolysis rate by a factor of three. However, the isotope distribution of the methanes and propylene in pyrolysis is different than for photolysis and much less reproducible. In our experiments the photolysis rate at 500° is nine times that for pyrolysis. From this ratio of rates and the values of the methane and propylene isotope ratios for photolysis and pyrolysis, we estimate that error in the photolysis ratios is about 10% at this temperature. At temperatures of 490° and lower, the pyrolysis rate is insignificant compared with the photolysis.

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(10) J. R. McNesby and A. S. Gordon, THIS JOURNAL, **79**, 825 (1957).

(11) A. Sehon and M. Szwarc, *Proc. Roy. Soc.* (*London*), **A202**, 263 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Photochemical Type II Process in 2-Hexanone-5,5-d_2 and 2-Hexanone[1]

BY R. SRINIVASAN

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The photolysis of 2-hexanone-5,5-d_2 at 3130 Å. and room temperature was found to give mainly C_3H_5D and acetone which was a mixture of CH_3COCH_2D (45%) and CH_3COCH_3 (54%). Since the course of the photolysis and the nature of the minor products were similar to that of 2-hexanone, it was surmised that acetone-d_1, which may have been formed in the type II primary process, was subsequently exchanging the odd deuterium atom for a hydrogen atom. Such an exchange was not found to take place after the photolysis and the exchanging molecule was most probably not any impurity in the parent ketone or the parent ketone itself. The photolysis of 2-hexanone in a cell that had been left in contact with D_2O vapor and then evacuated, gave rise to C_3H_6 and acetone which was made up of CH_3COCH_2D (25%) and CH_3COCH_3 (75%). Pure acetone did not exchange with the D_2O on the walls under the same conditions. These results can be explained on the basis of the formation of propylene and the enolic form of acetone in the primary process, and the subsequent rearrangement of the enolic form to the ketonic form on the walls, the latter step often involving the exchange of one hydrogen (or deuterium) atom.

Introduction

The photochemical process by which aliphatic ketones with at least one hydrogen atom on the carbon in the γ-position to the carbonyl group give rise to a methyl ketone and an olefin is classified[2] as type II to distinguish it from the primary processes which lead to free radicals. There is a considerable amount of indirect evidence that a γ-hydrogen is transferred to the α-carbon in the type II process.[3] Davis and Noyes[4] suggested that direct evidence might be obtained by replacing the γ-hydrogen atoms with deuterium in a ketone such as 2-hexanone and analyzing for the isotopic content of the photoproducts. The present study was undertaken with this in view.

The photolysis of 2-hexanone has been studied by Norrish and co-workers,[5] by Davis and Noyes,[4]

(1) This work was supported in part by Contract AF18(600)1528 with the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command. Reproduction in whole or in part is permitted for any purpose by the United States Government.

(2) This classification was proposed by C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935).

(3) A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954).

(4) W. Davis, Jr., and W. A. Noyes, Jr., THIS JOURNAL, **69**, 2153 (1947).

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