

TABLE V
PARTIAL PRESSURES OF SIGNIFICANT PRODUCTS IN EXIT GAS FROM TYPICAL EXPERIMENTS

Test	Operating pressure, atm.	Apparent contraction, %	Partial pressures, atm. ^a					Ratios of partial pressures ^b		
			H ₂	CO	H ₂ O	CO ₂	CH ₄	H ₂ O/H ₂	CO ₂ /CO	CH ₄ /(H ₂) ²
294	7.8	65	2.94	1.66	0.93	1.97	0.29	0.316	1.19	0.033
399	7.8	80	2.39	0.33	1.90	2.61	.56	.795	7.91	.098
342	21.4	65	7.98	5.24	2.10	5.42	.65	.263	1.03	.010
428	21.4	22	9.44	9.96	1.08	0.75	.17	.115	.007	.0019

^a Other gaseous components are present in minor amounts and are not included. Water is determined by difference and these values are slightly high. ^b Thermodynamic data: the oxidation of iron to magnetite at 250° requires H₂O/H₂ and CO₂/CO in excess of 0.025 and 2.2, respectively.⁸ Hydrogenation of graphite to methane requires CH₄/(H₂)² less than 1200. The free energy of formation of Hägg carbide at 250° is +3.7 kcal./mole.²⁶ Thus, oxidation or hydrogenation of the carbide should have a greater thermodynamic tendency than corresponding reactions with iron or graphite, respectively.

bility of the catalyst surface, as determined by product distribution, should be approximately equal for the reduced and the carbided catalyst. Surface areas of reduced, carbided or nitrided catalysts before synthesis are approximately equal.¹⁹

At pressures of 7.8–14.5 atm., the activity of carbides remained constant or increased with time, but at 21.4 atm. the activity of carbides decreased rapidly. Although the rapid decrease in activity at 21.4 atm. is probably related to the rapid oxidation and simultaneous destruction of the carbide and modification of the physical structure of the catalyst, the explanation is not simple. For example, the carbided catalyst used at 14.5 atm. had a constant activity even when more than 80% of the iron had been converted to magnetite. Similarly, although the reduced catalysts oxidize

(26) L. C. Browning, T. W. DeWitt and P. H. Emmett, *THIS JOURNAL*, **72**, 4211 (1950).

less rapidly at 7.8 atm. than at 21.4 atm., the activities at the lower pressure usually decrease with time (X152, Fig. 1) but remain essentially constant at the higher pressure (X515, Fig. 2). Thus, other factors, such as changes in physical structure accompanying oxidation, are probably important in determining catalytic activity. The activities of nitrided iron catalysts, which oxidize at a slower rate than corresponding reduced catalysts, remain essentially constant for long periods of synthesis.¹⁸

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Activation Energies of Reactions of Methyl Radicals with Organic Molecules¹

BY FRANCIS OWEN RICE AND ROBERT E. VARNERIN

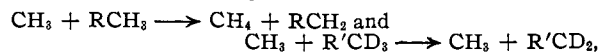
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We have decomposed 50-50 mixtures of two organic compounds one of which is fully deuterated and have determined initial values of the ratio [CH₄]/[CH₃D] or [CD₃H]/[CD₄] (depending on which compound was more stable) at different temperatures. We have assumed that these ratios give the relative speeds of reaction of either CH₃ or CD₃ with the respective compound. For example [CH₄]/[CH₃D] would be the relative speeds of the two reactions, CH₃ + RCH₃ → CH₄ + RCH₂ and CH₃ + R'CD₃ → CH₃D + R'CD₂ where RCH₃ and R'CD₃ are the two organic compounds. The relative activation energies were determined by plotting the logarithm of the ratio against 1/T. Our results are in good agreement with published measurements made in a much lower range of temperature.

In some recent work² in this Laboratory, we studied the thermal decomposition of mixtures of organic compounds in which one was the ordinary compound and the other was fully deuterated. For example when 50-50 mixtures of CH₃CHO and C₂D₆ are heated to about 500°, the products are methane and carbon monoxide, showing that the ethane suffers no perceptible decomposition into ethylene and hydrogen. However, the methane formed is not pure CH₄ but a mixture of CH₄ and most of the deuterated methanes. If one measures the ratio [CH₄]/[CH₃D] for different frac-

tional decompositions one can determine by extrapolation the ratio at the beginning of the reaction. Under proper conditions, such measurements give the relative speeds of two known elementary reactions at a given temperature; by varying the temperature, the difference of the activation energies of the two reactions may be obtained.

If we decompose a 50-50 mixture of two organic compounds, RCH₃ and R'CD₃ (R' being fully deuterated), the initial value of the ratio [CH₄]/[CH₃D] may be assumed to be the relative rates of the two elementary reactions



providing that CH₃ is a chain radical. The ratio [CH₄]/[CH₃D] can be conveniently measured if

(1) The work was supported in part by the United States Air Force under Contract No. AF-18(600)-64 monitored by the Office of Scientific Research.

(2) F. O. Rice and R. E. Varnerin, *THIS JOURNAL*, **75**, 324, 2629 (1954).

$R'CD_3$ is more stable than RCH_3 ; if the reverse is the case, we measure the ratio $[CD_3H]/[CD_4]$ and the same argument applies. Fortunately a great many organic compounds appear to decompose through a relatively long methyl radical chain so that we may neglect any formation of CH_4 or CH_3D by steps occurring at the beginning or end of the chain.

We have recently published³ a preliminary report of this work in which we measured the relative speeds of certain elementary reactions at a single temperature and found reasonably satisfactory agreement with results of other work done in a much lower temperature range and using a quite different technique.

McNesby and his co-workers⁴ have measured $[CD_3H]/[CD_4]$ ratios at different temperatures in the pyrolysis and photolysis of mixtures of acetone and acetone- d_6 and have concluded that the activation energy difference for the abstraction of deuterium and hydrogen from acetone by methyl- d_3 radicals is 1.67 kcal./mole.

In this paper we have made a rather large number of measurements on a wide variety of compounds and have compared our results with the published results of others using a quite different technique.

Experimental

In all experiments equimolar mixtures of RH and $R'D$ were prepared and decomposed at an initial pressure of 200 mm. and in the temperature range of 480 to 606°.

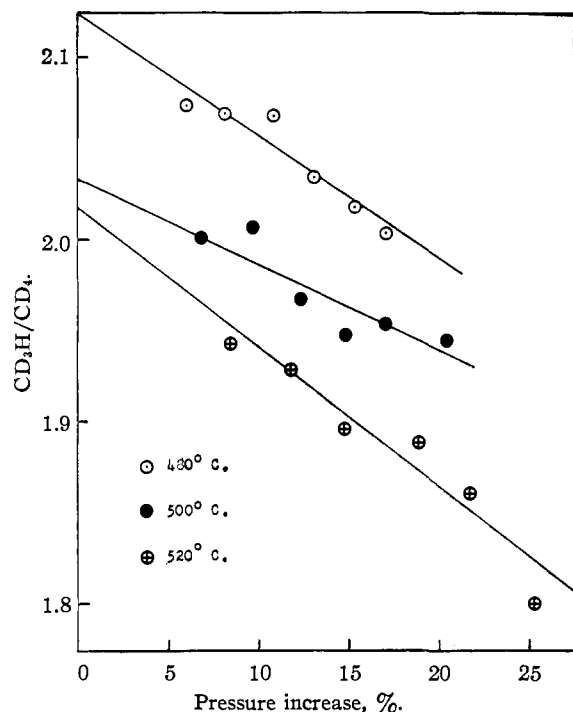


Fig. 1.—Thermal decomposition of equimolar mixtures of CH_3CHO and CD_3CDO at an initial total pressure of 200 mm.; mass spectrometer measurements: O, 480°; ●, 500°; ⊕, 520°.

(3) See ref. 2, p. 2632.

(4) (a) J. R. McNesby, T. W. Davis and A. S. Gordon, *THIS JOURNAL*, **76**, 823 (1954); (b) J. R. McNesby and A. S. Gordon, *ibid.*, **76**, 1416 (1954).

apparatus used in this work was the conventional static system described in a previous paper.²

The CD_3CDO was supplied as paraldehyde by Tracerlab, Inc. The paraldehyde was heated to 300° to form acetaldehyde- d_4 , the portion distilling from -78 to -95° being used in the experiments. The CD_3CDO was 98.3% deuterated. The CH_3CHO was prepared in a similar manner from J. T. Baker C.P. paraldehyde.

The C_2D_6 was a mixture of 97.7% C_2D_6 and 2.3% C_2D_5H . The C_2H_6 and CH_4 were Phillips research grade gases 99.3 and 99.8% pure, respectively. The propane, *n*-butane, isobutane, *n*-pentane, neopentane, and 2,3-dimethylbutane were Phillips pure grade with a minimum purity of 99%. The acetone was Mallinckrodt analytical reagent grade and only the fraction distilling from -78 to -195° was used in experiments. CH_3OCH_3 was supplied by Ohio Chemicals Co.; C_2H_4 and $CH_3CH=CH_2$ were Matheson C.P. grade gases.

The mass spectrometric analyses were made on a 90° sector field instrument employing magnetic scanning. The method of Schissler, Thompson and Turkevich⁵ has been employed for calculating the spectra of CH_3D , CH_2D_2 and CD_3H . The spectrum for CD_4 was obtained from a sample of CD_4 containing about 1% CD_3H .

Results

We studied the thermal decomposition, at several temperatures, of various organic compounds in presence of equimolar amounts of ethane- d_6 and also the thermal decomposition of acetaldehyde- d_4 in presence of various organic compounds. In general, the mixtures were decomposed for different fractional decompositions, and the methane fraction was separated and analyzed in the mass spectrometer. Under our conditions, the ethane- d_6 decomposed only to a very small extent as shown by the amounts of CD_4 and CD_3H (less than 2-3% of the total methanes). There were traces of CH_2D_2 , but the bulk of the gas consisted of CH_4 and CH_3D . In the case of the acetaldehyde- d_4 mixtures, usually the other organic compound decomposed to a very small extent and the bulk of the methane fraction consisted of CD_4 and CD_3H .

Our analyses were made at different fractional decompositions and the ratios $[CH_4]/[CH_3D]$ or $[CD_3H]/[CD_4]$ were obtained for the beginning of the reaction by extrapolating to zero decomposition. It seems desirable to obtain the ratio in this way partly because of possible complications due to the accumulation of reaction products and partly to avoid the necessity of introducing a correction because of the different speeds of the two reactions with methyl radicals. In Fig. 1 we show a graph for a mixture of acetaldehyde and acetaldehyde- d_4 . The slopes were determined by the method of least squares.

In our preliminary work we made a series of runs on 50-50 mixtures of various organic compounds with ethane- d_6 at a single temperature, 580°. Table I, column 1 contains the values of our $[CH_4]/[CH_3D]$ ratios extrapolated to zero time and column 2 of the same table contains calculated values of the ratios in column 1, based on published data performed in a much lower range in temperatures. We also measured the $[CH_4]/[CH_3D]$ values at different temperatures for several of these reactions and give the results in Table II. By plotting the $\log[CH_4]/[CH_3D]$ against $1/T$

(5) D. O. Schissler, S. O. Thompson and J. Turkevich, *Faraday Soc. Disc.*, **10**, 46 (1951).

TABLE I
MEASUREMENTS OF INITIAL $[\text{CH}_4]/[\text{CH}_3\text{D}]$ RATIOS IN THE THERMAL DECOMPOSITION OF MIXTURES OF ETHANE- d_6 AND VARIOUS ORGANIC COMPOUNDS AT 580°

RH	$[\text{CH}_4]/[\text{CH}_3\text{D}]^a$		Ref. ^b
	Our values	Calcd. ^b	
Propane	5.23 ± 0.20	3.9	
<i>n</i> -Butane	7.3 ± .6	5.5	39
		9.5	40
		8.1	40†
		7.5	39
Isobutane	8.1 ± 1.0	5.4	41
		2.7	42
		5.5	39
		3.7	39
<i>n</i> -Pentane	20.0 ± .08	5.5	39
Neopentane	4.36 ± .08	3.7	39
CH ₃ CHO	29.6 ± 1.5	72.3	49
CH ₃ COCH ₃	4.09 ± .20	8.7	50
		7.0	50†
		9.8	17
		6.6	52
		7.4	44
CH ₃ OCH ₃	10.4 ± .20	4.7	45
		12.8	7†

^a We interpret this as the relative speeds of the two reactions, $\text{CH}_3 + \text{RH}$ and $\text{CH}_3 + \text{C}_2\text{D}_6$, respectively. The errors were estimated by the method of least squares. ^b These calculated values are taken from a review by A. F. Trotman-Dickenson, *Quart. Rev.*, VII, 198 (1953), assuming that the activation energy of the reaction $\text{CH}_3 + \text{C}_2\text{D}_6 \rightarrow \text{CH}_3\text{D} + \text{C}_2\text{D}_5$ is 1.7 kcal. greater than for the reaction $\text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5$ and that the *A* factors are equal. The numbers in the last column are those in the *Quart. Rev.* article.

as well as calculated values. We also made measurements at different temperatures and calculated the activation energies as above assuming an activation energy⁶ of 7.8 kcal. for the reaction $\text{CD}_3 + \text{CD}_3\text{CDO} \rightarrow \text{CD}_4 + \text{CD}_3\text{CO}$.

Discussion

Our results, obtained by pyrolytic experiments in the temperature range 500–600°, are in fairly good agreement with values calculated from experiments done usually in the range 100–300° and in which radicals were often generated photochemically. We may assume therefore with some degree of confidence that whenever we have a chain reaction in which CH_3 is one of the chain carriers, we can measure the activation energy of the reaction $\text{CH}_3 + \text{substrate}$, with reference to some standard reaction such as $\text{CH}_3 + \text{C}_2\text{D}_6$ or $\text{CH}_3 + \text{CD}_3\text{CDO}$. With chain mechanisms, we may assume that all reactions at the beginning or end of the chain producing CH_4 or CH_3D may be neglected in comparison with their production in the chain itself. Of course, we must also assume that any molecular mechanism occurs only to a negligible extent since we have assumed that the methanes all come from methyl radicals.

Another possible source of error would be a special sort of exchange reaction between a methyl and a large chain radical. Ordinarily such collisions are chain ending steps and result in combination or disproportionation. In the decomposi-

TABLE II
MEASUREMENTS OF INITIAL $[\text{CH}_4]/[\text{CH}_3\text{D}]$ RATIOS IN THE THERMAL DECOMPOSITION OF MIXTURES OF ETHANE- d_6 AND VARIOUS ORGANIC COMPOUNDS AT DIFFERENT TEMPERATURES

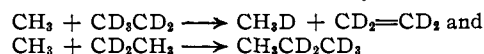
RH	Temp., °C.							<i>E</i> ^a	<i>E</i> ^b (lit.)	Ref. in T-D.
	530	540	550	570	580	600	610			
<i>n</i> -Pentane		21.3	20.9		20.0			9.9 ± 2.7	8.1	39
Neopentane				4.40		4.35	4.22	10.4 ± 2.2	10.0	39
CH ₃ CHO	34.8		32.5	30.7				7.9 ± 3.1	8.0	49
CH ₃ COCH ₃			4.20	4.06		3.96		10.1 ± 1.0	9.7	50
									9.6	50†
									9.5	17
									9.5	52
CH ₃ OCH ₃	10.74		10.54		10.38			11.1 ± 0.5	9.7	44
									8.8	45
									10.0	7†

^a The value of *E* was found by plotting $\log [\text{CH}_4]/[\text{CH}_3\text{D}]$ against $1/T$ and assuming $E = 12.1$ for the reaction $\text{CH}_3 + \text{C}_2\text{D}_6 \rightarrow \text{CH}_3\text{D} + \text{C}_2\text{D}_5$. The values given for the errors are crude estimates since we made measurements at only three temperatures. ^b These values are taken directly from a review of A. F. Trotman-Dickenson, *Quart. Rev.*, VII, 198 (1953).

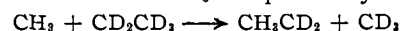
and assuming that the activation energy for the reaction $\text{CH}_3 + \text{C}_2\text{D}_6 \rightarrow \text{CH}_3\text{D} + \text{C}_2\text{D}_5$ is 12.1 kcal., that is 1.7 kcal. greater than Trotman-Dickenson's value for the reaction $\text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5$, we obtained the activation energies for the different reactions represented by the general equation $\text{CH}_3 + \text{RH} \rightarrow \text{CH}_4 + \text{R}$ and have compared these with values calculated from published data.

We then performed a second similar series of experiments in which we studied the thermal decomposition of 50-50 mixtures of acetaldehyde- d_4 and various organic compounds at 527°. Our results were similar and are shown in Table III

tion of a 50-50 mixture of ethane- d_6 we would have



However, it is possible that the following reaction might occur in which CH_3 is replaced by CD_3



(6) This value is rather uncertain. Dr. Trotman-Dickenson has pointed out to us an error in his review (see Table I, ref. b). The activation energy for the reaction $\text{CH}_3 + \text{CH}_3\text{CHO}$ is 7.5 kcal. according to the work of R. K. Brinton and D. H. Volman, *J. Chem. Phys.*, 20, 1053 (1952) and not 8.0 kcal., as reported in the review. Dr. E. W. R. Steacie (private communication) has informed us that Dr. P. Ausloos and he have found considerably lower activation energy for the reactions of methyl with acetaldehyde. We have adopted a value based on the latest published work.

TABLE III

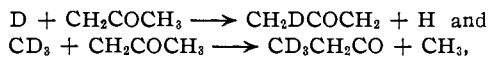
MEASUREMENTS OF INITIAL $[CD_3H]/[CD_4]$ RATIOS IN THE THERMAL DECOMPOSITION OF MIXTURES OF ACETALDEHYDE- d_4 AND VARIOUS ORGANIC COMPOUNDS AT 527°

RH	$[CD_3H]/[CD_4]^a$ Our values	Calc. lit. ^b	Ref. in T-D.
CH ₃ CHO	1.992 ± 0.012	2.24 ^c	
CH ₄	0.081 ± .007	0.026	38
C ₂ H ₆	.264 ± .004	.099	39
<i>n</i> -Butane	.676 ± .014	.215	39
		.374	40
		.303	40†
Isobutane	.64 ± .014	.305	39
		.220	41
		.115	42
<i>n</i> -Pentane	.84 ± .06	.221	39
Neopentane	.325 ± .006	.143	39
2,3-Dimethylbutane	.87 ± .04	.331	39
		.460	39
Ethylene	.095 ± .008	.115	43
CH ₃ CH=CH ₂	.417 ± .006	.171	43
CH ₃ COCH ₃	.488 ± .023	.325	50
		.266	51†
		.368	17
		.248	52
CH ₃ OCH ₃	.601 ± .011	.276	44
		.183	45
		.472	7†

^a We interpret this as the relative speeds of the two reactions CH₃ + RH and CD₃ + CD₃CDO, respectively. The errors were estimated by the method of least squares.

^b These calculated values are taken from a review by A. F. Trotman-Dickenson, *Quart. Rev.*, VII, 198 (1953), assuming that the activation energy of the reaction CD₃ + CD₃CDO → CD₄ + CD₃ + CO is 9.2 kcal., that is 1.7 kcal. greater than for the reaction CD₃ + CH₃CHO → CD₃H + CH₃ + CO and that the *A* factors are equal. ^c It is assumed that the relative speeds of hydrogen and deuterium abstraction from CD₃CDO and CH₃CHO is the same as from CD₃COCD₃ and CH₃COCH₃ (ref. 4).

By comparing results from different mixtures, especially those containing a reference substrate such as acetaldehyde where the large chain radical is exceedingly unstable, it should be possible to test if this effect is appreciable. Fortunately, the effect very probably does not appear in pyrolysis involving acetone and does not therefore affect the very careful measurements made by McNesby and his co-workers.⁴ If we consider the two reactions



the second is the only one of the two that would be expected to occur in the mechanism of the acetone decomposition; although the first reaction probably has a very low activation energy, the second reaction very probably has a high activation energy and may therefore be safely neglected.

Some preliminary experiments appear to indicate that the method outlined in this paper may be limited to the study of chain steps of the type CH₃ + substrate. For example we studied the thermal decomposition of 50-50 mixtures of ethane and ethane- d_6 and attempted to measure, in spite of rather formidable analytical difficulties, the initial ratios $[CH_4 + CH_4D]/[CD_4 + CD_3H]$. We hoped in this way to obtain the relative speed

TABLE IV

MEASUREMENTS OF INITIAL $[CD_3H]/[CD_4]$ RATIOS IN THE THERMAL DECOMPOSITION OF MIXTURES OF ACETALDEHYDE- d_4 AND VARIOUS ORGANIC COMPOUNDS AT DIFFERENT TEMPERATURES

RH	Temp., °C.			<i>E</i> ^a	<i>E</i> (lit.) ^b	Ref. in T-D.
	500	530	560			
Ethane	0.244	0.265	0.276	9.9	10.4	39
				±1.1		
<i>n</i> -Butane	.637	.682	.733	10.3	8.3	39
				±0.2	8.2	40
					9.5	40†
Isobutane	.622	.642	.680	9.0	7.6	39
				±0.6	7.3	41
					6.6	42
Neopentane	.301	.327	.357	10.8	10.0	39
				±0.2		
2,3-Dimethylbutane	.870	.870	.870	7.3	6.9	39
				±0.8	7.8	39
Ethylene	.095	.095	.095	7.3	10.0	43
				±1.0		
CH ₃ CH=CH ₂	.442	.447	.455	8.0	7.7	43
				±0.3		
CH ₃ COCH ₃		.486	.518	10.2	9.7	50
				±3.0	9.6	51†
					9.5	17
					9.5	52
CH ₃ OCH ₃	.567	.601	.668	10.8	9.5	44
				±1.0	8.4	45
	.480	.500	.520		10.0	7†
CH ₃ CHO	2.124	2.034	2.014	6.5	6.5 ^c	
				±0.3		

^a The value of *E* was found by plotting log $[CD_3H]/[CD_4]$ against $1/T$ and assuming *E* = 9.2 kcal. for the reaction CD₃ + CD₃CDO → CD₄ + CD₃ + CO. The values given for the errors are crude estimates since we made measurements at only three temperatures. ^b These values are taken directly from a review of A. F. Trotman-Dickenson, *Quart. Rev.*, VII, 198 (1953). ^c P. Ausloos and E. W. R. Steacie, private communication.

and relative activation energy of the two reactions C₂H₆ → 2CH₃ and C₂D₆ → 2CD₃ on the assumption that these two are the only sources of CH₃ and CD₃ and that all the CH₃ and CD₃ are converted directly into CH₄, CH₃D, CD₄ and CD₃H. We did not continue with this work partly due to the difficulty of interpreting the analytical data and partly because of the possibility that collision of the chain radicals (e.g., CH₃CH₂ + H = 2CH₃) would sometimes produce methyl radicals instead of ending the chain.

In this work we aimed at exploring the general possibilities of the method for measuring activation energies of elementary reactions. The method is somewhat laborious because in order to obtain a high degree of precision, measurements must be made at a number of different temperatures and the result for any one temperature is obtained by a number of mass spectrometric analyses for different fractional decompositions and an extrapolation to zero decomposition. We did not attempt to obtain a high degree of precision in any of our experiments and made measurements on a rather wide variety of compounds at only three temperatures. However we feel that this method can be developed to a point where it would be possible to measure certain activation energy differences perhaps to ±0.1 kcal. The limitations of the method seem to be that it is confined to the chain step involving attack of methyl on the substrate.

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