A high temperature nozzle for introducing samples into the gas diffraction camera over the range from room temperature up to 160° is described.

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[A Contribution from the Chemical Laboratories of Harvard University]

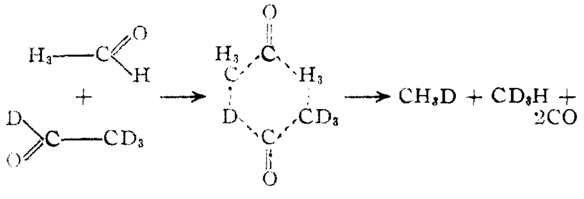
The Thermal Decomposition of Acetaldehyde

By J. Carrell Morris

Recent studies on the mechanism of the thermal decomposition of acetaldehyde into carbon monoxide and methane have indicated that the reaction proceeds, at least in part, by means of a reaction chain involving free radicals. Thus Burton, Ricci and Davis[1] were able to demonstrate that radio-lead was transported in a Paneth-type experiment in which acetaldehyde was decomposed under normal conditions. This undoubtedly showed the presence of free radicals in their experiments. Rice and Polly[2] and later, in a more extensive fashion, Smith and Hinshelwood[3] found that the normal thermal decomposition was inhibited by the addition of propylene to the gaseous acetaldehyde in the reaction vessel. These studies on inhibition, generally considered a very reliable test for the detection of radical chain reactions, led to an estimate that a minimum of about $^2/_3$ of the reaction occurred by means of free-radical chains.

In an attempt to confirm this conclusion and perhaps to check on more detailed phases of the mechanism of the reaction a somewhat different approach to the problem was devised. Mixtures of ordinary acetaldehyde and acetaldehyde-d_4 were allowed to decompose together and the resulting products were analyzed as to the isotopic composition of the methanes formed.

Such a determination might be expected to give a rather intimate knowledge of actual processes occurring in the reaction. For, if the decomposition were an intramolecular one, then the CH_3CHO could give just CH_4 and CO, while CD_3CDO would yield only CD_4 and CO. Consequently, if this mechanism were operative, the analysis should show none of the partially deuterated methanes. If the decomposition were a bimolecular one, then reactions of the type



should occur, yielding CD_3H and CH_3D as well as CH_4 and CD_4. One would not anticipate finding CH_2D_2, however. In the third plausible case, if the reaction took place by a chain mechanism, processes of the type

$$CH_3 + CD_3CDO = CH_3D + CD_3 + CO$$
$$CD_3 + CH_3CHO = CD_3H + CH_3 + CO$$

would be expected to produce CD_3H and CH_3D and perhaps also CH_2D_2, if the reactions were more complicated than those illustrated.

So, while it might not be possible by this method to distinguish between the latter two possibilities, such an analysis should certainly provide evidence differentiating the first possibility from the other two.

Benedict, Morikawa, Barnes and Taylor[4] have shown that such mixtures of the isotopic methanes may be analyzed readily by means of their infrared spectra. In particular, the absorption in the range 1000–1500 cm.$^{-1}$ is very characteristic of the particular isotopic methanes present in a mixture and their relative proportions. In the present study this method of analysis was followed by measuring the infrared absorption over the range 1000–1500 cm.$^{-1}$ of the samples of gas obtained from the decomposition of the mixtures of acetaldehyde and acetaldehyde-d_4. The results obtained led to the conclusion that the thermal decomposition of such mixtures produced CH_4 and CD_4 almost exclusively.[5] This is definite evidence that, contrary to the findings of previous authors,[1,2,3] the decomposition of acetaldehyde proceeds mainly by a unimolecular mechanism.

Confirmation for this point of view was obtained by an analysis of data on the absolute rate of the thermal decomposition of acetaldehyde. During the course of the present research it was noted that the rate of decomposition of "pure" acetaldehyde was materially decreased if the aldehyde were treated with hydroquinone and freshly distilled from it before use. The rates found after such treatment were considerably lower than the "normal" rates of Smith[6] or of Smith and Hinshelwood[3] and approached the "inhibited" rates found by the latter authors. A reasonable conclusion is that the positive indications of a chain reaction found in this decomposition were caused by a superimposed induced process initiated by an impurity.

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[1] M. Burton, J. E. Ricci and T. W. Davis, This Journal, **62**, 265 (1940).

[2] F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938).

[3] J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc.* (London), **A180**, 237 (1942).

[4] W. S. Benedict, K. Morikawa, R. B. Barnes and H. S. Taylor *J. Chem. Phys.*, **5**, 1 (1937).

[5] J. C. Morris, This Journal, **63**, 2535 (1941).

[6] R. E. Smith, *Trans. Faraday Soc.*, **35**, 1328 (1939).

Experimental.—The acetaldehyde was an Eastman Kodak Co. product which was purified further by several distillations in the vacuum system from baths at 0° to baths at −80°. During the series of distillations the acetaldehyde was several times outgassed by causing ebullition while the bulb containing the liquid was connected directly to the vacuum pump. In addition the aldehyde was twice frozen in liquid air and pumped out to 10^{-5} mm. to remove any final traces of oxygen, which is known to accelerate the reaction.[7] Attempts to purify the acetaldehyde by distillation from a dry-ice bath to a liquid-air bath were unsuccessful because of the formation of the white, solid polymer which has been observed before under the same conditions.[8] The vapor pressure of the final material at 0° checked that given in the literature[9] within a few mm. and remained substantially constant during the use of 80% of the liquid. This material is called the "untreated" sample.

A portion of the above sample was further purified by distilling it into a bulb containing some solid hydroquinone crystals and allowing it to remain there for several days. It was then distilled off from the hydroquinone in small samples just before use. This latter is called the "treated" sample and gave a rate of decomposition only one-half to one-third as great as the previous material.

The deuteroacetaldehyde came from two sources. First runs were made on a sample prepared from C_2D_2 and D_2O by slight modification of the method of Zanetti and Sickman,[10] while later a quantity of 99.5% deuteroacetaldehyde was purchased from Norsk Hydro. Each was subjected to the same purification procedure as the CH_3CHO, the final samples having a vapor pressure at 0° which checked that given by Zanetti and Sickman.[10] Both samples were shown to contain better than 99% C—D bonds by means of their infrared absorption spectra.[11]

With the deuteroacetaldehyde also subsequent treatment with hydroquinone was found to give a sample which decomposed more slowly than the untreated sample, but the decrease in this case was not nearly as marked, and additional treatments failed to lower the rate any further.

The decompositions were carried out in a cylindrical Pyrex vessel of approximately 300-ml. capacity, which had an outside diameter of about 5 cm. and was mounted snugly in a cavity bored in an aluminum block of 10-cm. diameter. The block was wound with insulated resistance wire and was surrounded by several inches of magnesia insulation. To maintain the block at 500° a current of about 3 amperes was required. The reaction vessel was connected by means of capillary tubing to a three-way stopcock and to a variable-level mercury manometer, which gave a total dead space amounting to less than 1 ml.

By passing the heating current through a voltage controller such a uniform heating was obtained that temperatures constant within 0.5° could be maintained indefinitely and no additional temperature regulation was necessary. The temperature was measured with a two-junction thermocouple inserted in a well of 8-mm. glass tubing which ran into the center of the reaction vessel. The thermocouple was standardized against boiling sulfur and by comparison with a Bureau of Standards platinum resistance thermometer at several temperatures.

For the infrared analyses the reacted mixture of gases was allowed to expand into a 300-ml. bulb which had its lower end chilled in dry-ice to condense any unreacted acetaldehyde. Usually, however, this was an unnecessary precaution, for the mixtures were generally allowed to react completely before withdrawing them from the reaction vessel. It was not necessary to eliminate the carbon monoxide since it does not absorb in the portion of the spectrum used. The sample of methanes and carbon monoxide was then transferred by means of a Töpler pump to the infrared absorption cell, which was 30 cm. in length and 2.5 cm. in diameter with plane rock salt ends cemented on with Apiezon wax. This was attached to the apparatus by a ground glass joint so that it could be transferred easily to the spectrograph. Ordinarily the cell was filled with 200 mm. of the carbon monoxide–methanes, corresponding to 100-mm. pressure for the methanes present. This pressure was found empirically to give the most suitable amount of absorption for the significant frequencies.

The spectrograph used was the one described by Gershinowitz and Wilson.[12] It was necessary to use only the rock salt prism to obtain the 1000–1500 cm.$^{-1}$ spectra with sufficient precision. The technique of measurement and recording of the spectra was the same as that outlined in the Gershinowitz and Wilson paper.

I am grateful to Prof. E. Bright Wilson for permission to use the spectrograph for these analyses.

Results of Infrared Analyses.—A number of preliminary spectra were determined to ascertain the exact results to be expected from various possibilities. First, the spectrum for the case of no mixing of the methanes was measured by mixing 100 mm. of $CD_4 + CO$ from the decomposition of CD_3CDO alone with 100 mm. of $CH_4 + CO$ from the decomposition of CH_3CHO and determining the infrared spectrum for the mixture. The absorption spectrum obtained is shown as curve I of Fig. 1. The significant features of this curve are the double absorption maximum caused by the CD_4 at 990 and 1035 cm.$^{-1}$, the double maximum caused by CH_4 at 1305 and 1350 cm.$^{-1}$ and the absence of appreciable absorption in between. If there were partially substituted

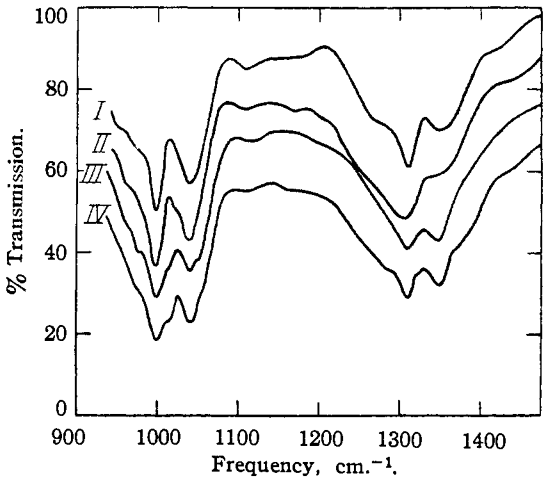

Fig. 1.—Infrared absorption spectra of methanes resulting from the decomposition of acetaldehyde and acetaldehyde-d_4: (I) prepared mixture of 100 mm. of $CH_4 + CO$ and 100 mm. of $CD_4 + CO$; (II) two hundred mm. of 1:1 mixture of $CH_4 + CO$ with $CD_4 + CO$ which has been heated for five days at 500° (scale is displaced downward 10%); (III) two hundred mm. of mixture formed by decomposition of 215 mm. of CH_3CHO in presence of 400 mm. of $CD_4 + CO$ (scale is displaced by 20%); (IV) two hundred mm. of mixture formed by decomposition of 183 mm. of CD_3CDO in presence of 370 mm. of $CH_4 + CO$ (scale is displaced by 30%).

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(7) M. Letort, *Compt. rend.*, **197**, 1042 (1933).

(8) M. Letort, *ibid.*, **202**, 767 (1936).

(9) R. Gilmour, *J. Soc. Chem. Ind.*, **41**, 293 (1922).

(10) J. E. Zanetti and D. V. Sickman, THIS JOURNAL, **58**, 2034 (1936).

(11) J. C. Morris, *J. Chem. Phys.*, **11**, 230 (1943).

(12) H. S. Gershinowitz and E. B. Wilson, *ibid.*, **6**, 197 (1938).

deuteromethanes present, there should be additional maxima of absorption at 1160 cm.$^{-1}$ for CH_3D, at 1090 and 1235 cm.$^{-1}$ for CH_2D_2 and at 1290 cm.$^{-1}$ for CHD_3.[4]

Since it is known that traces of oxygen will induce a chain reaction in the decomposition of acetaldehyde,[13] it was concluded that a representation of the absorption curve to be expected if the thermal reaction occurred by a chain mechanism might be obtained by analyzing the sample obtained from decomposing a mixture of the aldehydes in the presence of a trace of oxygen. Accordingly, 148 mm. of CD_3CDO, 150 mm. of CH_3CHO and 0.05 mm. of oxygen were mixed and allowed to react overnight at a temperature of 435°. The temperature was chosen low enough to make the ordinary thermal reaction negligible. When a sample of the products was subjected to infra-red analysis, curve VII in Fig. 2 was obtained. The expected maxima listed above are all apparent, some of them occurring with great intensity. The appearance of the maximum at 1090 cm.$^{-1}$ for CH_2D_2 means that the chain processes are more complicated than the simple ones listed in the introduction to the paper.

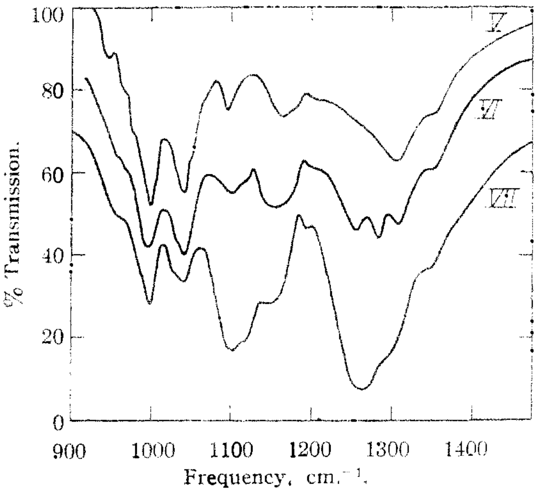

Fig. 2.—Infrared absorption spectra of methanes resulting from the decomposition of mixed acetaldehyde and acetaldehyde-d_4: (V) two hundred mm. of mixture formed by decomposition of 145 mm. of "treated" CD_3CDO with 152 mm. of "treated" CH_3CHO; (VI) two hundred mm. of mixture formed by decomposition of 209 mm. of "untreated" CD_3CDO with 239 mm. of "untreated" CH_3CHO (scale displaced by 10%); (VII) two hundred mm. of mixture formed by decomposition of 150 mm. of CH_3CHO, 148 mm. of CD_3CDO and 0.05 mm. of O_2 (scale displaced by 30%).

A run was now made to make sure that if mixed deuteromethanes were found in the later experiments, they had resulted from processes taking place in the actual decomposition of the acetaldehydes and not from side exchange reactions. A sample consisting of 206 mm. of CH_4 + CO and 203 mm. of CD_4 + CO was heated in the reaction vessel at 500° for five days to test whether the methanes would exchange among themselves at this temperature. The spectrum of a sample taken at the end of this time is shown as curve II of Fig. 1. The increased absorption between 1200 and 1300 cm.$^{-1}$ indicates the formation of a small amount of CHD_3, but the exchange has been very slight, as indicated by the general similarity of the curve with curve I.

It was still possible, however, that exchange might take place between molecules of acetaldehyde and of methane. Or, if there were methyl radicals present as a result of chain processes, the reactions

$$CH_3 + CD_4 = CH_3D + CD_3$$
$$CD_3 + CH_4 = CD_3H + CH_3$$

might have complicated the conclusions. Therefore, two additional preliminary runs were carried out. In the first, 215 mm. of CH_3CHO was allowed to decompose completely at 480° in the presence of 400 mm. of CD_4 + CO, obtained from the previous decomposition of 201 mm. of CD_3CDO. In the second the process was reversed and 183 mm. of CD_3CDO was allowed to decompose completely at the same temperature in the presence of 370 mm. of CH_4 + CO, obtained from the decomposition of 189 mm. of CH_3CHO. The absorption spectra of samples taken from these runs are shown in curves III and IV, respectively. Both indicate only slight exchange and therefore reactions of the type shown above will not affect the conclusions to be drawn from the mixed decomposition experiments.

Curves V and VI in Fig. 2 show the results of the spectroscopic analysis of the methanes resulting from the decomposition of mixtures of CH_3CHO and CD_3CDO. For curve VI a mixture of 209 mm. of "untreated" CD_3CDO and 239 mm. of "untreated" CH_3CHO was allowed to react for two days at 480°, after which it was transferred to the absorption cell and analyzed. A marked increase in absorption in the 1100–1300 cm.$^{-1}$ range over that shown in curves I–IV is noted. Pronounced maxima are found at 1100, 1160, 1260 and 1290 cm.,$^{-1}$ showing the presence of all of the partially deuterated methanes and indicating that chain processes had been instrumental in the decomposition in this instance.[14] However, none of the maxima for the intermediate deuteromethanes are as strong as those obtained in curve VII for the reaction induced by oxygen. Hence, it is probable that only a portion of the reaction proceeded by means of the chain mechanism. This is in accord with the results of other

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(13) M. Letort, *J. Chim. Phys.*, **34**, 428 (1937).

(14) This result offers some experimental verification for the proposition that the reaction CH_3 + CH_3CHO is a much faster process than CH_3 + CH_4, since the reactions which yielded the samples for curves III and IV, which showed no exchange, were also carried out with the "untreated" aldehydes. (See "The Aliphatic Free Radicals," F. O. Rice and O. K. Rice, Johns Hopkins Press, 1935, for an estimate of the relative rates.)

workers on the nature of the "normal" decomposition of acetaldehyde.[1,2,3]

In contrast curve V shows the absorption spectrum of the sample resulting from the reaction together of 145 mm. of "treated" CD_3CDO and 152 mm. of "treated" CH_3CHO at 542°. The temperature is not of major importance, for an almost identical curve was obtained from a similar mixture decomposed at about 480°. It can be seen that the absorption between 1100 and 1300 cm.$^{-1}$, while greater than that for curves I–IV, is nevertheless much less than that for curve VI, indicating a much smaller amount of chain reaction in this case. By a comparison of curve V with curve VII, assuming that the latter represents 100% chain reaction, it may be concluded that not more than 10–20% of the reaction with the "treated" aldehydes proceeded by means of a chain mechanism. Because of the difficulty in obtaining perfectly pure acetaldehyde, even by means of the treatment with hydroquinone, it seems likely that the residual 10% of chain reaction may have resulted from a slight remainder of induced chain reaction, and that the decomposition of acetaldehyde itself is completely a molecular reaction.

Results on the Rate of Decomposition of Acetaldehyde.—Table I presents a summary of experiments on the absolute rate of decomposition of CH_3CHO, both before and after treatment with hydroquinone, along with a comparative tabulation of the results of other researches.[3,6,13,15] For the "untreated" acetaldehyde the rates check the values calculated from the results of Smith for the "normal" decomposition of acetaldehyde. It was for samples like these that the infrared experiments showed a considerable amount of chain reaction, perhaps 50%, and the inhibition experiments of Smith and Hinshelwood[3] pointed to 60–70% of chain reaction. However, the second part of Table I shows that these rates can be considerably decreased by further purification. The absolute rates after treatment with hydroquinone are equal to about half the values for the "normal" reaction of Smith and are reduced almost to the values recorded by Smith and Hinshelwood for the completely inhibited reaction. The results of Letort, who used a very rigid purification procedure, are also lower than those of Smith or of the present untreated samples, although they are not as low as the rates for the "treated" samples in the present study. However, they constitute additional evidence that thoroughly purified acetaldehyde decomposes at a slower rate than previously supposed. The implication is that the more rapid rates are caused by traces of impurity which initiate a chain reaction.

In addition there is evidence here that the slower rates represent a molecular reaction in agreement with the infrared analyses. For, the inhibited rates of Smith and Hinshelwood presumably signify a suppression of all chain reaction, leaving a residuum which is entirely a molecular reaction. Moreover, the results in the second part of Table I demonstrate that it is possible to reduce the rate of reaction almost to this minimum point without the use of inhibitors in the reaction vessel. Consequently this too must represent a reaction which is almost entirely molecular.

TABLE I

THE RATE OF THERMAL DECOMPOSITION OF ACETALDEHYDE

		Initial rates of decomposition, mm./min.			
			Smith and Hinshelwood		
Temp., °C.	Orig. pres., mm.	This study	Normal[a]	Inhibited[b]	Letort[c]
	(a)	Before treatment with hydroquinone			
445	309	2.1	1.7	0.65	1.1
477	67	0.9	0.57	0.21	0.42
478	118	1.6	1.46	.54	1.05
478	240	5.6	4.85	1.8	3.07
478	309	7.0	7.2	2.8	4.50
478	479	13.3	15.0	5.9	8.60
494	302	12.0	14.3	5.4	8.5
	(b)	After treatment with hydroquinone			
484	107	1.1	1.6	0.6	1.2
484	186	2.1	4.0	1.5	2.7
484	328	5.2	10.2	3.9	6.3
542	313	40	97	35	49

[a] These figures were calculated from the results of R. E. Smith (ref. 6) by the following procedure. Since the values tabulated by Smith were found to conform to the relation $-dx/dt = kx^{1.6}$, the half-life times were converted to initial rates by the equation: initial rate, $R = 1.15t_{50}/p_0$. Then large-scale plots of log R against $1/T$ were constructed and values of R at the required temperatures for a number of different pressures were read off from the straight line relationships. These values of R were used to evaluate k at each temperature in the table, and from these latter the rates at the specific pressures in the table were computed from the first equation above. It is estimated that errors of calculation should be certainly less than 10%. [b] The values in this column were calculated from the data of J. R. E. Smith and C. N. Hinshelwood (ref. 3) by the same method as (a). [c] Computed from the equation $-dx/dt = kx^{1.5}$, where $k = 4.44 \times 10^{12}e^{-46{,}000/RT}$ (moles/liter)$^{-1/2}$ min.$^{-1}$, given by M. Letort (refs. 13, 15).

In Table II are shown similar results on the decomposition of CD_3CDO. In this instance the reduction in rate after treatment with hydroquinone was a maximum of about 20%. As in the previous table the "untreated" results agree with those calculated from the data of Smith, while the "treated" values are lower.

It is of interest to speculate on the nature of the impurity which causes the acceleration in these decompositions. Some qualitative observations have been made. It was found that in a series of duplicate runs the rates of successive runs would gradually tend to increase as more and more of the liquid acetaldehyde in the storage reservoir was used up. This pointed toward an accelerant which was less volatile than the acetaldehyde and therefore could not have been gaseous oxygen. It was also noted that even following the treatment with hydroquinone to remove the impurity, the rate of decomposition of samples of the acetaldehyde was

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(15) M. Letort, *J. Chim. Phys.*, **34**, 265 (1937).

TABLE II

RATE OF THERMAL DECOMPOSITION OF ACETALDEHYDE-d_4

Temp., °C.	Orig. press., mm.	Initial rates of reaction, mm./min. This study	Smith[a]
(a) Before treatment with hydroquinone			
478	188	0.90	1.2
478	316	3.0	2.8
478	334	3.3	3.1
478	387	4.2	3.9
483	94	0.60	0.46
483	214	1.5	1.8
483	277	3.0	2.8
483	298	3.5	3.1
(b) After treatment with hydroquinone			
484	293	3.1	3.1
493	295	4.3	4.8
509	193	4.7	5.0
542	70	3.4	3.8
542	122	7.9	9.4
542	210	18.7	22.7
542	302	33.6	40.2

[a] Calculated by same method as values in Table I from paper of R. E. Smith (ref. 6).

again accelerated when the liquid acetaldehyde was allowed to stand after distillation from the hydroquinone. The formation of either an autoxidation product or a polymerization product of the acetaldehyde as the substance responsible for the accelerating chain reaction would account for this result. The cause of the effectiveness of hydroquinone in removing the impurity was not discovered, though it may be connected with its reducing power.

The amount of impurity necessary to produce such an acceleration is very small. Chain lengths of 4000 have been reported by Letort[13] in the oxygen accelerated reaction at this temperature. If the same chain length held in the induced reaction under consideration, then less than 0.1% of impurity would be needed to triple the rate of reaction. Few physical tests can detect the presence of this quantity of material.

The fact that the rate of decomposition of deuteroacetaldehyde was not subject to the same rapid acceleration as the ordinary acetaldehyde may be accounted for in a number of ways. One would be that the rate of formation of impurity is considerably smaller in CD_3CDO than in CH_3CHO so that there was a lesser quantity of the impurity present to cause acceleration. Or, the quantity of accelerant may have been about the same, but the rate of the induced reaction compared to the rate of the molecular reaction may have been smaller for the heavier isotope.

Discussion.—Both approaches to the problem of the mechanism of the thermal decomposition of pure acetaldehyde lead to the same conclusion that the reaction takes place substantially through a molecular process. However, a further conclusion may be drawn from the infrared analyses. The meager formation of intermediate deuteromethanes in the reaction of the pure mixed aldehydes provides definite evidence for the first of the possible reaction mechanisms mentioned earlier—the decomposition of individual particles of acetaldehyde to give methane and carbon monoxide in a single act. This means that the reaction must be truly unimolecular.

One might picture the operation of such a mechanism as an amplification of the normal bending vibration frequency of acetaldehyde in which the aldehyde hydrogen and the methyl group vibrate toward one another by means of a decrease in the C–C–H angle, while the carbonyl group recedes sufficiently to maintain the balance of the system. In discussing the spectrum of acetaldehyde this frequency has been called the "H-wagging frequency,"[11] since the hydrogen atom contributes most of the motion because of its lightness.

The dependence of the rate of reaction on concentration, however, is intermediate between a first-order and a second-order relation. This is another example of the common phenomenon that the kinetic order of a chemical reaction may not tell us its fundamental mechanism. A probable reason for such a difference in this case is that the rate of activation of acetaldehyde molecules by collision is not sufficiently rapid to maintain an equilibrium concentration of the activated species as it decomposes. This implies that the decomposition of the activated acetaldehyde molecules must be fast enough so that a sizable fraction will have decomposed before they have a chance to become deactivated by subsequent collision. The rate of activation of the molecules by collision then becomes a rate-determining step of comparable magnitude to the rate of decomposition of the activated molecules. If this is the case experiments with purified acetaldehyde at very high pressures should show a first-order relation and at very low pressures the reaction should become more nearly second order.

Insufficient experiments were performed in these researches to determine a kinetic equation for the decomposition of the completely purified acetaldehyde with any certainty.

Although the absolute rate is smaller, the dependence on concentration and the activation energy seem to be quite similar to those of previous kinetic studies. Consequently, one might obtain a satisfactory equation either by multiplying the constant factor in the equation of Letort[15] by 0.75 or by adopting the equation given by Smith and Hinshelwood[8] for the completely inhibited reaction as that for the decomposition of pure acetaldehyde.

The present data give a different value for the relative rates of decomposition of light and heavy acetaldehyde from that recorded by Smith.[6] Over a wide set of conditions he found a ratio for the rate of reaction of CH_3CHO to that of CD_3CDO of about 2.4. However, since the rate of reaction of the CH_3CHO was decreased by treatment much more than that of the CD_3CDO, it means that the true ratio must be lower. As in the case of the kinetic equation, no accurate evaluation of this ratio is possible because of the lack of sufficiently extensive figures, but they indicate that the value over the temperature range of the present experiments is 1.3–1.4.

Summary

1. The thermal decomposition of mixtures of acetaldehyde and acetaldehyde-d_4 has been carried out and the resulting methanes have been analyzed by means of their infrared absorption spectra. The results indicate that the thermal decomposition of acetaldehyde is a true unimolecular reaction and that chain processes play a very minor part, if any.

2. This conclusion has been confirmed by studies on the absolute rate of the thermal decomposition of acetaldehyde, which show the true rates to be only half as great as those previously observed.

3. The relative rate of thermal decomposition of acetaldehyde to that of acetaldehyde-d_4 is approximately 1.3–1.4.

CAMBRIDGE, MASS. RECEIVED DECEMBER 3, 1943

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Quinoidation of Triaryl Compounds—Hydroxyphenylbiphenylcarbinols

BY LEIGH C. ANDERSON AND W. A. FISHER[1]

Previous papers from this Laboratory[2] have presented data on the absorption spectra of several hydroxytriarylcarbinols and the corresponding fuchsones. A comparison of the absorption spectra of colored carbinols, of triphenylmethyl salts[3] and of triphenylmethyl[4] with those of quinone and the fuchsones indicated the existence of quinonoid structures for all these substances. Quinone, the free radical in ether solutions and the quinonoid carbinols have quinonoid bands which are low when compared to the corresponding bands in the fuchsones, the free radical in sulfur dioxide, and the triphenylmethyl salts. No attempt has yet been made to give an interpretation for the difference. This investigation presents data on triarylcarbinols wherein *p*-biphenyl groups have replaced one or both of the unsubstituted phenyl groups of *p*-hydroxytriphenylcarbinol. The absorption spectra obtained from these carbinols appear to offer an explanation for the variation in height of the quinonoid bands.

Two biphenylhydroxyphenylcarbinols have been studied: 4-hydroxy-4′-phenyltriphenylcarbinol and 4-hydroxy-4′,4″-diphenyltriphenylcarbinol. They were made by the condensation between phenol and *p*-biphenyldichlorophenylmethane and di-*p*-biphenyldichloromethane, respectively. Unless the correct conditions are adhered to, this condensation produces diphenoxymethane and tetraphenylmethane derivatives as chief products. The carbinols were also made by the aluminum chloride demethylation of the methoxy derivatives which were prepared by the reaction between *p*-anisylmagnesium bromide and 4-phenylbenzophenone and 4,4′-diphenylbenzophenone, respectively. The monobiphenylcarbinol was isolated in two forms: an intensely colored yellow form and a colorless modification. The dibiphenylcarbinol was isolated in two yellow modifications: one intensely colored and one which was considerably lighter in color. The fuchsone of each carbinol was prepared also.

The ultraviolet absorption spectra of ether solutions of these compounds show that a broad high band replaces the double band in the benzenoid portion of the spectrum when a *p*-biphenyl group is substituted for one of the phenyl groups of 4-hydroxytriphenylcarbinol (Fig. 1). This band is very similar to the one obtained from an hexane solution of biphenyl and is due, undoubtedly, to the biphenyl group in the carbinol. That its maximum is about 0.3 unit higher and its position about 200 mm.$^{-1}$ further toward the visible are effects easily attributable to the presence of the carbinol substitutent on the biphenyl. A second *p*-biphenyl group substituted in the carbinol merely increases the height of this band, emphasizing its source in the biphenyl groups.

The change in benzenoid absorption when a phenyl group in 4-hydroxytriphenylcarbinol is replaced by a biphenyl group seems to indicate that the biphenyl group acts as a unit in producing absorption and not as two phenyl groups. The absorption spectra of molecules containing both phenyl and biphenyl groups show that the phenyl absorption is completely blotted out beneath the biphenyl band (Figs. 1 and 2). The fact that the only appreciable change in this biphenyl band upon the introduction of more biphenyl groups into the molecule is in its height (Figs. 1 and 2) shows that each biphenyl group is acting more or less independently in producing the absorption

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[1] The material presented in this and the following paper constitutes a portion of a dissertation submitted by Willis Allan Fisher to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements of the Ph.D. degree, February, 1940.

[2] Anderson and Gomberg, THIS JOURNAL, 50, 204 (1928); Anderson, *ibid.*, 51, 1889 (1929); Anderson and Geiger, *ibid.*, 54, 3058 (1932).

[3] Anderson, *ibid.*, 52, 4567 (1930).

[4] Anderson, *ibid.*, 57, 1673 (1935).