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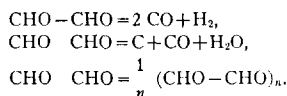


The Kinetics of the Decomposition of Gaseous Glyoxal

E. W. R. STEACIE, W. H. HATCHER AND J. F. HORWOOD, *Physical Chemistry Laboratory, McGill University*

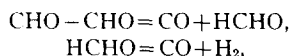
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The decomposition of gaseous glyoxal has been investigated from 410° to 450°C. The reaction is homogeneous and first order. Considerable carbon and tar is deposited, however, and the results are erratic. The following three reactions occur to about the same extent:

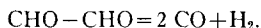


The results are discussed from the point of view of the occurrence of glyoxal as an intermediate in the oxidation of acetylene.

GLYOXAL has frequently been postulated as a product of the oxidation of gaseous organic compounds. It has been definitely shown to be present in considerable quantities during the oxidation of acetylene.¹ It has been suggested that the primary step in the acetylene oxidation is the formation of glyoxal, which then either oxidizes further or decomposes. Although, as far as we are aware, no investigation of the thermal decomposition has ever been made, it has always been assumed that it occurs as follows:²



giving the overall reaction



The present investigation was therefore undertaken (a) because of the interest attaching to the decomposition of simple molecules, (b) to fill an experimental gap in the Bone "hydroxylation" scheme for the oxidation of gaseous organic compounds, and (c) in connection with an investigation of the acetylene oxidation now in progress in this laboratory.

EXPERIMENTAL

Rates of reaction were followed by admitting the reactants to a heated Pyrex bulb, and ob-

serving the rate of pressure increase at constant volume by means of a capillary manometer. The apparatus was similar to one which has been previously described.³ The reaction vessel was heated by means of an electric furnace, the temperature being controlled by the hand regulation of rheostats. The temperature could be maintained constant to within 0.5°C. Temperatures were measured with a chromel-alumel thermocouple in conjunction with a thermocouple potentiometer. The connecting tubing between the reaction vessel and the manometer was maintained at 100°C by means of an electrical heating element to prevent condensation.

The preparation of pure gaseous glyoxal is complicated by the fact that it polymerizes readily to solid paraglyoxal, and the polymerization is not directly reversible. The gas was prepared in the usual way by heating paraglyoxal (Schuchardt) with phosphorus pentoxide.⁴ Considerable dehydration and charring occurs, however, and the gas is contaminated with a large amount of carbon monoxide. It was found that if the gas were condensed at -80° it froze out as the monomer, and it was possible to pump off foreign gases. If the solid monomer were heated to room temperature for a short time it evaporated with very little polymerization. During the course of the investigation the glyoxal was therefore stored as a solid at -80°, and was only warmed up when a sample of gas was to be withdrawn. Blank experiments showed that no com-

¹ Kistiakowsky and Lenher, *J. Am. Chem. Soc.* **52**, 3785 (1930); Spence and Kistiakowsky, *ibid.* **52**, 4837 (1930); Lenher, *ibid.* **53**, 2962 (1931).

² See, for example, the reference 1 and also Bone, *Proc. Roy. Soc. A* **137**, 243 (1932); *J. Roy. Soc. Arts* **81**, 550 (1933).

³ Hatcher, Steacie and Howland, *Can. J. Research* **7**, 149 (1932).

⁴ Harries and Temme, *Ber.* **40**, 165 (1907).

plication was introduced by polymerization in the connecting tubes.

It should be mentioned at the outset that the reaction is complicated by the deposition of carbon, tar, etc., and that in consequence the results obtained are rather erratic. It is therefore impossible to investigate the reaction with very high accuracy, but sufficient results have been obtained to establish the main features of the process.

THE PRODUCTS OF THE REACTION

If the reaction proceeds according to the mechanism given above, we should have a pressure increase of 200 percent at completion, since formaldehyde would decompose at the temperatures used. Actually, however, the average pressure increase at completion was about 90 percent. Some typical values are given in Table I.

TABLE I. *The pressure increase accompanying the reaction.*

Temp. (°C)	Percent pressure increases
450	93.0, 83.8, 85.3, 103.0, 94.5, 86.6
440	87.4, 93.2, 89.4, 92.5, 93.2, 94.0, 101.2, 94.7
430	73.5, 71.1
420	82.2

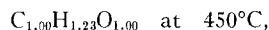
The gaseous products of the reaction were analyzed in a Burrell gas analysis apparatus, hydrogen being determined by combustion. Almost all the condensable substances (glyoxal, water, etc.) condensed out in the process of sampling. A small amount of material (always less than 1 percent) was absorbed in the KOH burette. It is very unlikely that this could be carbon dioxide, and it was assumed to be a trace of glyoxal or other condensable material. In any event the error which might be involved is negligible. In order to refer the gaseous products found back to the initial amount of glyoxal from which they came, it is necessary to know the amount of condensable material present in the mixture being sampled. This was done in the usual way by adding a known amount of nitrogen to the glyoxal before the reaction, and then determining nitrogen in the gaseous products. The results of analyses of this kind are given in Table II.

The main conclusion to be drawn from the

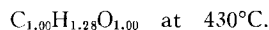
table is that the gaseous products of the reaction consist entirely of hydrogen and carbon monoxide, the amount of carbon monoxide being much greater than that of hydrogen. With decreasing temperature the H_2/CO ratio decreases to some extent. The carbon monoxide formed is approximately equal to the glyoxal disappearing.

In the case of analyses at the half-way stage it is difficult to draw conclusions regarding the amount of condensable material formed, on account of the uncertainty as to how much glyoxal has decomposed. At completion, however, it is possible to deduce the amount of condensable products with fair accuracy. At 450°C the amount is only slightly greater than that of hydrogen, while at 430° it is more than twice as much. The significance of this will be discussed later.

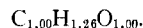
It is possible from the above analytical data to draw up a material balance for C, H and O, and hence to deduce the composition of the condensable material. Too much reliance cannot be placed in such balances, since all the errors involved in the reaction measurements and analyses accumulate in the result. If such a balance is made for all the analyses at completion, we obtain for the average composition of the condensable products



and



Or, on the average,



THE MECHANISM OF THE REACTION

It has previously been assumed² that the glyoxal decomposition proceeds simply as

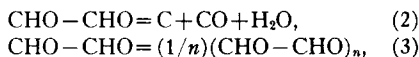


formaldehyde being completely decomposed at the temperatures used. It is obvious that such a simple scheme cannot hold, since (a) carbon and tar are formed, (b) the pressure increase at completion is only 90 percent instead of 200 percent, (c) a large amount of condensable products are formed, (d) the H_2/CO ratio is only 0.2 to 0.3 instead of 0.5.

Other obvious possibilities are:

TABLE II. *The products of reaction.*

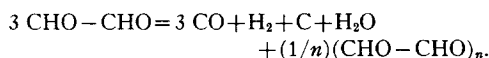
Temp. (°C)	% pressure increase when sample was taken	Moles per 100 moles initial glyoxal (including unchanged glyoxal, if any)			
		CO	H ₂	Condensable	H ₂ /CO
450	50	41.6	15.0	93.4	0.36
450	50	46.0	17.1	86.9	0.37
450	50	48.6	14.3	87.1	0.29
450	Completion	94.2	41.5	48.1	0.44
450	"	107.6	30.9	56.0	0.29
450	"	90.0	40.3	56.3	0.45
430	50	56.8	14.7	78.5	0.26
430	50	54.0	16.7	79.3	0.31
430	Completion	85.6	21.6	66.3	0.25
430	"	78.0	25.4	67.7	0.33
410	50	46.8	10.7	92.5	0.23
410	50	57.6	13.3	79.1	0.23
410	50	54.6	11.9	83.5	0.22



where $(\text{CHO}-\text{CHO})_n$ represents a polymer or condensable substance or substances of higher molecular weight than glyoxal, with approximately the same empirical composition.

It is not possible to account for the gaseous products on the basis of reactions (2) and (3) alone. On account of the fact that both CO and H₂ are formed, it appears probable that reaction (1) occurs to a considerable extent. A simple combination of (1) and (2) could be made to yield the correct H₂/CO ratio, but such a combination would give a pressure increase far too high (about 150 percent). A simple combination of (1) and (3) would give the correct pressure increase, but could not yield a H₂/CO ratio very different from 0.5.

Provided that reaction (3) gives rise to little gaseous material, a combination of reactions (1), (2) and (3) will account satisfactorily for the experimental results. Thus if we assume that all three reactions occur to the same extent, we have for the overall reaction



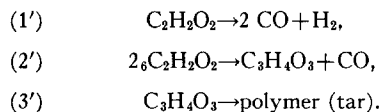
This accounts for the main facts, thus:

- (a) The CO formed is equal to the glyoxal decomposing,
 (b) The H₂/CO ratio is 0.33,
 (c) If we assume that n is about 3, the pressure increase at completion will be approximately 80 percent,

- (d) The composition of the condensable product is
 $\text{C}+\text{H}_2\text{O}+\text{C}_2\text{H}_2\text{O}_2=\text{C}_{1.00}\text{H}_{1.33}\text{O}_{1.00}$,
 which is in good agreement with experiment.

It appears therefore that the three reactions are of about equal importance.

An investigation of the photochemical decomposition of glyoxal has been carried out.⁵ The reaction was bimolecular, about 1.5 percent of the initial glyoxal decomposing to CO and H₂, and the remainder yielding CO and glycerosone (C₃H₄O₃). This is essentially a polymerization, similar to reaction 3, but splitting out CO. Norrish and Griffiths state that glycerosone decomposes at 200°C. Hence it is not likely that it is of importance here. It is, however, possible to account for the experimental results on the basis of a mechanism such as:



Considering the fact that large amounts of carbon are deposited, in addition to tarry materials, the first mechanism seems much more plausible.

The diminution of the H₂/CO ratio with decreasing temperature and the corresponding increase in the proportion of the condensable products must be due to a change in the balance between reactions 1 and 2, reaction 1 predominating at the higher temperature.

⁵ Norrish and Griffiths, J. Chem. Soc. 1928, 2829-40.

THE RATE OF REACTION

In view of the complicated nature of the reaction as outlined above, and of the fact that carbon and polymerized materials are formed, it is hardly to be hoped that the kinetics of the reaction can be very accurately established. Actually, the results obtained are decidedly erratic. It is possible, however, to infer the main characteristics of the reaction with some certainty.

The complete data for a typical experiment are given in Table III. It will be seen that excellent first order constants are obtained. This was

TABLE III. Data for a typical experiment.

Temperature 440°C			Empty reaction vessel	
Time (min.)	Pressure (cm)	Pressure increase (cm)	Percent reaction	(first order), min. ⁻¹
0	11.70	0.00	0.0	—
1	12.70	1.00	9.2	0.041
2	13.70	2.00	18.4	0.044
3	14.60	2.90	26.6	0.045
5	16.10	4.40	40.5	0.045
7	17.30	5.60	51.5	0.045
10	18.80	7.10	65.3	0.046
13	19.80	8.10	74.4	0.046
18	21.00	9.30	85.4	0.046
25	21.80	10.10	92.8	0.046
30	22.10	10.40	95.5	0.045
35	22.30	10.60	97.3	0.045
40	22.50	10.80	—	—
45	22.60	10.90	—	—
55	22.60	10.90	—	—

invariably true throughout the investigation, in spite of the erratic nature of the absolute rate.

The effect of temperature and of the glyoxal pressure on the rate of reaction is shown by Table IV. As a measure of the rate we have used $T_{12.5}$ and T_{25} , i.e., the times for the pressure to increase by 12.5 and 25 percent, respectively.

On account of the erratic nature of the results, it is not possible to determine the activation energy with any degree of accuracy. From the mean values of $T_{12.5}$ and T_{25} at higher pressures we obtain the value $E = 54,000 \pm 10,000$ cal.

It will be seen from Table IV that the times for a given fractional pressure increase are roughly independent of the initial pressure, and hence the reaction is apparently first order, insofar as the effect of pressure on the rate is concerned. The results, however, are too erratic to permit of accurate conclusions.

The last 7 runs listed above were made in a vessel packed with short lengths of 3/16 inch Pyrex tubing, the surface-volume ratio being about three times greater than that for the empty bulb. It is apparent that packing the bulb has very little influence on the rate, and the reaction is therefore homogeneous.

DISCUSSION

As we have seen, the results are rather erratic, and the reaction is far from an ideal one from the

TABLE IV. Reaction rate data.

Initial pressure, (cm)	$T_{12.5}$, (min.)	T_{25} , (min.)	Initial pressure, (cm)	$T_{12.5}$, (min.)	T_{25} , (min.)	Initial pressure, (cm)	$T_{12.5}$, (min.)	T_{25} , (min.)	Initial pressure, (cm)	$T_{12.5}$, (min.)	T_{25} , (min.)
Empty vessel 410°C						16.55	1.7	3.6	7.95	1.3	3.3
17.15	4.6	10.8	10.95	7.5	14.6	13.30	1.3	2.8	6.30	2.3	4.4
14.10	7.6	15.8	9.55	6.8	14.6	13.05	1.2	2.7	4.75	2.0	3.7
12.70	9.6	20.3	7.85	5.9	13.3	11.70	1.5	3.0	4.45	3.3	6.0
11.65	9.1	20.1	6.90	8.5	17.2	10.30	1.5	3.2	4.30	2.9	6.3
						9.90	1.4	2.8			
Empty vessel 420°C						Empty vessel 450°C					
11.55	7.0	14.6	9.05	7.4	15.0	22.15	0.6	1.4	10.0	1.2	2.5
10.30	6.4	13.5	7.80	5.8	13.4	21.70	1.1	2.2	4.05	1.8	4.3
9.95	5.8	12.1	6.40	7.6	—	15.50	1.1	2.4	3.30	1.4	3.3
						10.40	1.1	2.2			
Empty vessel 430°C						Packed vessel 430°C					
20.85	2.1	4.2	10.65	2.9	6.6	18.55	4.1	7.9	13.70	2.9	6.4
17.45	2.5	5.3	8.40	3.0	7.4	15.10	2.3	5.1	11.35	2.8	6.3
16.05	3.4	7.4	5.90	2.6	9.3						
Empty vessel 440°C						Packed vessel 450°C					
20.60	1.4	2.1	8.30	1.1	3.0	12.45	1.0	2.1	7.90	0.7	1.6
17.75	1.1	2.4	8.05	1.9	4.6	10.60	1.2	2.8			

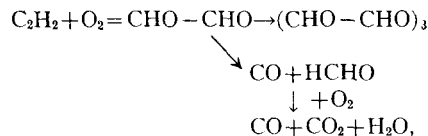
kinetic standpoint. The main interest in the results, however, lies in the fact that previous assumptions regarding the simple nature of the glyoxal decomposition have been shown to be incorrect.

In the oxidation of acetylene no appreciable quantity of carbon or tar is formed.^{1, 6} It therefore follows that while glyoxal may be formed and *oxidized* in the acetylene oxidation, it cannot *decompose* during the course of this reaction as has been previously assumed.

It also follows that the scheme proposed by

⁶ Steacie and McDonald, unpublished work.

Lenher for the oxidation of acetylene catalyzed by the oxides of nitrogen, *viz.*:



is not a possible mechanism, although certain *ad hoc* modifications could be made to bring it into line with the present work.

An investigation of the glyoxal oxidation is in progress.

MAY, 1935

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Orientation Effects in Bimolecular Ionic Reactions

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(Received January 15, 1935)

It is shown on the basis of accepted views concerning second order ionic reactions in solution that the variation with concentration of the electrostatic orientation effects in such a reaction arising from the lack of symmetry of a spheroidal ion is negligible in dilute solution. Deviations from Brönsted's law must be attributed to other causes.

IT has been observed that certain bimolecular ionic reactions deviate very considerably from the requirements of the limiting Brönsted formula, which is, for water as solvent and at 25°C,

$$\log k'' = \log k_0 + z_1 z_2 (\mu)^{\frac{1}{2}}. \quad (1)$$

In this equation k'' is the observed bimolecular specific reaction rate, k_0 is a quantity independent of concentration, z_1 , z_2 are the valences of the reacting ions, and μ is the ionic strength. In many instances these deviations are probably due to failure of the simple Debye-Hückel limiting law for ions of high valence, but there are a few cases where this explanation cannot hold. Outstanding among these is the one observed by LaMer and Kamner.¹ These authors found that the reaction between α -bromopropionate and thiosulfate ions follows the Brönsted formula accurately, while the analogous reaction involving the β -bromopropionate ion leads to a slope of the

$\log k''$ vs. $(\mu)^{\frac{1}{2}}$ curve which does not even have the expected sign. After an exhaustive study had indicated that the effect is not due to side-reactions or other such causes, LaMer and Kamner suggested that purely electrostatic effects resulting from a comparatively large separation of charge and center of reaction (the bromine atom) in the unsymmetrical organic ion might lead to the observed results. It is the purpose of the present note to examine this suggestion a little more closely. It will appear from the study of a fairly general case that this explanation is not valid, if one accepts present views concerning second order ionic reactions in solution.

Christiansen² developed a statistical theory of bimolecular ionic reactions which he showed to be in formal agreement with Eq. (1) in very dilute solutions. His treatment led to a general result which may be written

$$k'' = k_0 \exp(-\epsilon z_2 \varphi_1 / kT) \cdot \Omega \cdot (1 + \sum \chi_i f_i). \quad (2)$$

¹ LaMer and Kamner, J. Am. Chem. Soc. **53**, 2832 (1931).

² Christiansen, Zeits. f. physik. Chemie **113**, 35 (1924).