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The Kinetics of the Oxidation of Gaseous Glyoxal

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The kinetics of the oxidation of gaseous glyoxal have been investigated at 220°C. The reaction occurs by a chain mechanism, the rate being dependent upon roughly the second power of the aldehyde concentration, and independent of oxygen provided the oxygen concentration is not too low. The wall factor in the breaking of chains

is not very pronounced, but the condition of the surface is of importance in the initiation of the chains. The main products of the reaction are CO, CO₂, H₂O and glyoxylic acid. The results are satisfactorily expressed by the mechanism of aldehyde oxidation previously proposed by Steacie, Hatcher and Rosenberg.

INTRODUCTION

THE oxidation of acetylene has been the subject of a considerable number of investigations, but the interpretation of the results obtained is still a matter of doubt. In the mechanisms which have been proposed glyoxal has been given a prominent place, since it has been frequently shown to be produced in considerable quantities.¹ For this reason it seemed to be advisable to investigate the decomposition and oxidation of glyoxal, since no data were available on its behavior. The results of the investigation of the decomposition have already been reported,² and the present paper deals with the kinetics of the oxidation.

The oxidation of glyoxal is also of interest by comparison with the behavior of acetaldehyde,³ and of propionaldehyde.⁴

EXPERIMENTAL

The experimental method was identical with that of the previous investigation, except that since lower temperatures were required an oil bath was substituted for the electric furnace. The aldehyde and oxygen were mixed within the reaction vessel rather than outside it, since it had been found in the case of other aldehydes that incipient oxidation occurs even at room temperature.

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

² Hatcher, Horwood and Steacie, *J. Chem. Phys.* **3**, 291 (1935).

³ Bodenstein, *Zeits. f. physik. Chemie* **B12**, 141 (1931); Hatcher, Steacie and Howland, *Can. J. Research* **5**, 648 (1931); **7**, 149 (1932); Pease, *J. Am. Chem. Soc.* **55**, 2753 (1933).

⁴ Steacie, Hatcher and Rosenberg, *J. Phys. Chem.* **38**, 1189 (1934).

THE PRESSURE CHANGE ACCOMPANYING THE REACTION

The reaction differed from the acetaldehyde and propionaldehyde oxidations in that instead of a decrease in pressure corresponding to the formation of a stable peracid, followed by a gradual increase in pressure at the end of the reaction, there was an increase throughout until a constant value was reached. The maximum pressure increases for typical experiments are shown in Table I. In most cases they represent the final pressure, which remained constant for from 1 to 15 hours. For the lower temperatures these values remain constant with varying oxygen/aldehyde ratio, but at 220°C there is a tendency to drift, which has very little apparent connection with the composition of the mixture, though when the oxygen/aldehyde ratio is lower than about 2 the pressure increases have a somewhat lower mean value. The significance of the pressure increase will be discussed later in connection with the mechanism of the reaction.

TABLE I. Pressure increase at completion.

T°C	O ₂ CHO·CHO	INITIAL GLYOXAL PRESSURE (cm)	ΔP EXPRESSED AS % OF INITIAL GLYOXAL
150	2.13	11.50	28.3
150	1.68	11.90	29.8
200	2.74	14.45	43.9
200	1.05	14.25	42.8
220	3.82	12.00	91.2
220	3.78	9.00	78.9
220	3.22	15.00	83.7
220	2.95	11.95	85.3
220	2.94	8.95	81.5
220	2.74	12.10	90.0
220	2.26	15.10	86.7
220	1.83	12.10	81.5
220	1.75	12.00	67.9
220	1.65	12.10	72.7
220	1.54	12.10	71.5
220	1.29	12.00	75.8

THE PRODUCTS OF THE REACTION

The gaseous products of the reaction were withdrawn and analyzed as described in the previous paper. The first few analyses showed no hydrogen, and no combustions were done thereafter. The data for the actual analyses are given in Table II, and are recalculated in terms

TABLE II. Gas analyses. Temperature 220°C.

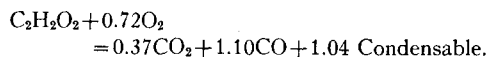
EXPT. No.	INITIAL MIXTURE (cm)			GASEOUS PRODUCTS (%)			
	CHO. CHO	O ₂	N ₂	O ₂	N ₂	CO	CO ₂
1	12.10	18.55	17.30	25.2	38.2	28.4	8.2
2	12.10	22.20	11.80	28.6	27.2	29.9	14.3
3	12.00	25.48	6.57	43.8	16.3	31.2	8.7
4	12.00	20.99	10.96	32.3	28.3	30.8	8.6
5	12.00	24.19	5.06	37.9	12.6	37.2	12.3
6	12.00	45.87	5.38	57.5	8.6	25.1	8.8
7	11.95	35.30	14.35	44.6	24.4	23.5	7.5
8	12.10	19.95	27.35	23.2	47.6	22.0	7.2

TABLE III. The products of the reaction.

EXPT. No.	O ₂ CHO. CHO	% ΔP AT COM- PLETION	MOLES PER 100 MOLES INITIAL GLYOXAL				
			O ₂ USED	CO	CO ₂	CON- DENS- ABLE	CO/CO ₂
1	1.54	71.5	58.9	106.2	30.8	93.2	3.45
2	1.83	81.5	80.9	107.0	51.2	103.9	2.09
3	2.12	67.1	65.0	105.0	29.0	98.0	3.62
4	1.75	67.9	70.7	99.3	27.7	111.6	3.58
5	2.02	88.3	75.0	124.0	41.0	97.7	3.02
6	3.82	91.2	82.0	131.0	46.0	96.7	2.85
7	2.95	85.3	76.0	115.6	36.9	109.1	3.22
8	1.65	72.7	70.0	89.8	29.3	123.8	3.06

of the initial glyoxal in Table III. The method of determining the condensable matter was, as before, that of adding nitrogen. It will be seen that there is good agreement among the analyses in view of the smallness of the samples available.

The average values for the eight analyses give the following overall equation for the reaction:



The average CO/CO₂ ratio is 2.98, and the average pressure increase 78 percent. From a material balance of this equation the empirical formula of the condensable material is found to be C_{0.53}H₂O_{1.60}.

To reconcile the possible products of the reaction with this formula it is necessary to assume that the carbon oxides are the result of complete combustion, so that the amount of

water in the condensable material is half their sum. This leaves a residue of C_{0.53}H_{0.53}O_{0.88}. An obvious possibility on chemical grounds is glyoxylic acid, which has the formula, on the basis of the carbon above, C_{0.53}H_{0.53}O_{0.80}, and thereby satisfies the analyses almost perfectly.

The material balance offers little or no indication of a peroxidized end product, or of substances containing a higher proportion of oxygen than glyoxylic acid. The reaction bulb was cut down at the end of a run and an aqueous solution of the condensable products subjected to qualitative tests. It was strongly acid, gave a negative test for peracids with potassium iodide, and a negative reaction with Fehling's solution. The mercuric oxide test for formic acid gave a faint cloudiness hardly to be associated with metallic mercury, and was therefore considered to be negative. A decidedly positive test for glyoxylic acid was obtained by reversing the usual Hopkins-Cole test for tryptophane. It was found, however, that trimeric glyoxal reacts in the same way, and a trace of polymer might therefore be responsible for the positive result. However, since the test responded immediately, though it frequently took as long as 15 minutes with the reactants, and since the solution was strongly acid to litmus, it appears reasonable to accept the result of the test, at least as a partial verification of the inferences drawn from the material balance.

A blank run with glyoxal alone at the same temperature and for the average time to completion showed a pressure decrease due to polymerization of only three percent of the initial glyoxal. Under conditions of oxidation this would be considerably less, and may be quite safely ignored.

We can therefore account for the stable products empirically by assuming that glyoxal is oxidized directly or indirectly to glyoxylic acid, which is then largely oxidized completely to CO, CO₂ and water. The kinetic interpretation of the results will be discussed later.

THE RATE OF THE REACTION

Complete data for some typical experiments are given in Table IV. The reaction shows a small induction period, as is usually the case in oxidation reactions.

TABLE IV. Data for typical experiments.

O ₂ /CHO·CHO	2.94	2.68	1.68
P _{CHO·CHO} , cm	8.95	9.95	11.90
TEMPERATURE	220°C	220°C	150°C
REACTION VESSEL	Empty	Packed	Empty
TIME, (min.)	% ΔP	TIME, (min.)	% ΔP
0	0.0	0	0.0
2	1.7	3	2.5
4	4.5	6	3.5
8	11.2	9	7.0
10	15.6	16	12.6
16	26.3	23	16.6
34	49.8	38	22.1
49	59.3	49	24.6
79	69.4	90	30.2
109	74.4	159	34.2
192	80.5	214	34.7
214	81.5	869	41.7

The rate of the reaction has been inferred from the rate of change of pressure. It is therefore necessary to show that under varying conditions a given pressure increase corresponds to the same amount of reaction. There are several indications that this is the case. In the first place, although the final pressure increases are rather erratic, there is no systematic variation with changing oxygen/glyoxal ratio. Secondly, the analyses at completion are in satisfactory agreement, and it therefore appears that the final result is the same no matter what relative concentrations of oxygen and glyoxal are used. That the course of the reaction is also the same is indicated by the fact that the form of the pressure-time curves does not change with changing oxygen/glyoxal ratio. Further confirmation is furnished by some analyses which were made when the pressure increase was 50 percent relative to the initial glyoxal. With oxygen/glyoxal ratios of 2.52, 2.18, 1.31 and 0.70 the CO/CO₂ ratios were sensibly constant, viz. 4.8, 4.6, 4.7 and 4.3. Thus it appears that at least the relative amounts of CO and CO₂ formed at any stage of the reaction are not appreciably dependent on the oxygen/glyoxal ratio. It therefore seems justifiable to use the time for the pressure to change from a 20 percent to a 40 percent increase as a measure of the rate of the reaction, and the data in Table V are reported in this manner.

At the beginning of a series of experiments with a new reaction vessel there was a pronounced surface aging effect, the velocity of the

TABLE V. Reaction velocity data. Temperature 220°C, unpacked reaction vessel.

GLYOXAL, (cm)	O ₂ , C ₂ H ₂ O ₂	T ₄₀ -T ₂₀ , (min.)	GLYOXAL, (cm)	O ₂ , C ₂ H ₂ O ₂	T ₄₀ -T ₂₀ , (min.)
20	2.27	7.1	15	0.81	10.8
20	1.87	7.3	10	3.44	10.2
20	1.63	6.9	10	2.24	10.4
20	1.59	6.7	10	1.67	9.9
20	1.19	7.5	10	1.45	11.0
20	0.93	7.5	10	1.26	11.5
20	0.89	8.3	10	2.74	10.5
20	0.78	8.8	10	2.39	10.9
20	0.61	11.8	5	4.00	15.5
20	0.53	11.3	5	3.22	15.5
15	2.77	8.3	5	2.89	15.6
15	2.36	8.1	5	2.41	17.2
15	1.92	8.2	5	2.11	18.4
15	1.33	8.4	5	2.09	18.5
15	1.07	8.0	5	1.94	21.5
15	0.96	9.4			

reaction increasing from run to run. It was usually necessary to make about 30 runs before reproducible results could be obtained. The data in Table V were obtained after the reaction vessel had reached a steady condition.

The effect of pressure

It will be seen from the above table that with glyoxal pressures of 20, 15 and 10 cm the rate is independent of the oxygen concentration provided that the oxygen/glyoxal ratio is greater than 1. The falling off in rate when the ratio is too low is hardly a real effect, since there is no longer sufficient oxygen for complete reaction. At the lowest glyoxal pressure (5 cm), however, the rate becomes dependent on the oxygen concentration when the oxygen/glyoxal ratio falls below about 2.5. By plotting the logarithms of the glyoxal pressures against the logarithms of $T_{40}-T_{20}$ we obtain a value for the order of the reaction of 1.6. Hence, except when the oxygen concentration is too low, we can express the rate by

$$-(d/dt)(C_2H_2O_2) = K(C_2H_2O_2)^{1.6}.$$

The effect of temperature

It is evident from the pressure increases at completion listed in Table I that the course of the reaction changes greatly with changing temperature. Under the circumstances it is hardly worth while determining the temperature coefficient, and measurements have therefore been confined to 220°C.

The effect of surface and of foreign gases

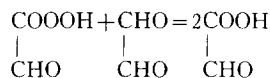
A number of experiments were made with a reaction vessel packed with short lengths of 3/16-inch Pyrex tubing which had been subjected to the same process of cleaning as the empty bulb. The packed bulb had a surface-volume ratio 5 to 6 times greater than the empty bulb. The reaction was slowed down considerably (about 50 percent), and there was a profound change in its course, the pressure increase at completion amounting to only 30 to 40 percent, and the CO/CO₂ ratio of the gaseous products being reduced from 3.0 to 1.7. It is apparent that the later stages of the reaction must be considerably altered. The magnitude of the retarding effect is not great, however, compared with other oxidation reactions, and it appears that the wall is not the major factor in breaking the reaction chains. This conclusion is supported by the experiments made with added nitrogen (Table V). It will be seen that no appreciable acceleration of the reaction is produced by the foreign gas, although such an acceleration would be expected if the majority of the chains were broken at the wall.

DISCUSSION

The kinetic characteristics of the oxidation of glyoxal are strikingly similar to those of acetaldehyde, of propionaldehyde, and of oxidation reactions in general. The induction period, the dependence of the rate upon the aldehyde concentration to about the second power and its independence of oxygen, as well as the pronounced influence of the condition of the surface show that it must unquestionably occur by a chain mechanism. With acetaldehyde and propionaldehyde the chain carrier is an activated peracid, which is moderately stable after deactivation and appears among the condensable products at the end of the reaction, its formation leading to a decrease in pressure. With glyoxal an analysis in the induction period showed that some 30 percent of the average total oxygen consumption had occurred after three minutes of reaction, and a very small quantity of carbon monoxide was formed. It appears therefore that the mechanism is very similar to that of the other aldehydes. Glyoxal, however, is a com-

paratively unstable aldehyde, and it is not surprising to find that the intermediate chain carriers do not appear in the end products to any great extent. The reaction is therefore characterized by an increase in pressure, which is greater the higher the temperature. Formaldehyde⁵ behaves in the same way.

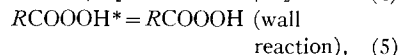
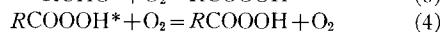
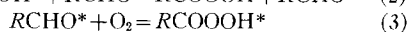
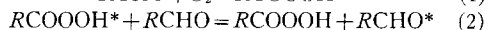
The glyoxylic acid formed in the reaction probably arises by



since peracids do not normally decompose to give the corresponding acid. The oxides of carbon may be assumed to arise in the usual way by the subsequent oxidation and decomposition of the primary products. The fact that the CO/CO₂ ratio decreases as the reaction proceeds, and that more CO₂ is formed in a packed reaction vessel indicates that the secondary processes leading to the formation of the oxides of carbon are at least partially heterogeneous.

That both aldehyde groups are not oxidized to the carboxylic structure is in agreement with the results of Hatcher and Holden,⁶ who found no trace of oxalic acid during the oxidation of glyoxylic acid by hydrogen peroxide in aqueous solution.

The kinetic results are in excellent agreement with the mechanism proposed by Steacie, Hatcher and Rosenberg for the oxidation of gaseous aldehydes. Thus we have



whence we obtain

$$-(d/dt)(RCHO) = K_1 K_2 (RCHO)^2 (O_2) / (K_4 (O_2) + K_5).$$

As we have seen, the wall effect is not large, but is nevertheless appreciable. Hence when the

⁵ Fort and Hinshelwood, Proc. Roy. Soc. **A129**, 284 (1930); Askey, J. Am. Chem. Soc. **52**, 974 (1930).

⁶ Hatcher and Holden, Trans. Roy. Soc. Can. (3) **19**, 11 (1925).

oxygen concentration is large K_w is negligible compared to $K_1(\text{O}_2)$, and the above expression reduces to

$$-(d/dt)(R\text{CHO}) = K_1 K_2 (R\text{CHO})^2,$$

in agreement with experiment. On the other hand, we would expect that at low oxygen concentrations K_w would no longer be negligible,

and that the rate would become dependent upon a power of the oxygen concentration lower than the first. Actually the data of Table V show that when the partial pressure of oxygen falls below about 10 cm the rate begins to fall off in the manner indicated above.

The bearing of these results upon the oxidation of acetylene will be discussed in a forthcoming publication.

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The Polarizability and Related Properties of Molecular Hydrogen and the Diatomic Hydrogen Ion

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The polarizability of molecular hydrogen is calculated from both the Rosen and the Wang eigenfunctions by the variational method. The eigenfunctions of the perturbed molecule contain two parameters which are adjusted to give the molecule a minimum energy. The Rosen eigenfunction leads to a parallel polarizability $7.5 \times 10^{-25} \text{ cm}^3$ and a perpendicular polarizability $7.4 \times 10^{-25} \text{ cm}^3$. The Wang eigenfunction gives similar results. When only one adjustable parameter is used in the variational method, the

formula for the polarizability is $\alpha = 8(\bar{q}_1^2 + \bar{q}_1 \bar{q}_2) a_0^3$ where q_1 and q_2 are the coordinates of electrons 1 and 2 in the direction of the applied electric field and a_0 is the radius of the first Bohr orbit of atomic hydrogen. The magnetic susceptibility and the mean square dimensions of the hydrogen molecule are computed. It is found that the Kirkwood formula is applicable to the diatomic hydrogen ion and polarizabilities are obtained for many internuclear separations using the Guillemin and Zener eigenfunction.

THE recent papers of Steensholt¹ have renewed interest in the problem of calculating the polarizability of molecular hydrogen. In 1932, we computed the polarizabilities by applying the variational method of Hylleraas² and Hassé³ upon the Rosen⁴ and Wang⁵ eigenfunctions. The eigenfunctions for the perturbed molecule were considered in both the one parameter form: $\psi_0[1 + A(q_1 + q_2)]$ and the two parameter form: $\psi_0[1 + A(q_1 + q_2) + B(r_1 q_1 + r_2 q_2)]$. Where ψ_0 is the eigenfunction of the unperturbed molecule. A and B are parameters to be varied so as to give the system a minimum energy; q_1 and q_2 are the coordinates of electrons one and two in the direction of the applied electric field as measured from the center of the molecule; r_1 and r_2 are their distances from the center of

the molecule. The numerical results are presented in Table I and compared with the values obtained by Mrowka⁶ and by Steensholt.¹ Mrowka formed approximate eigenfunctions for the excited states of the hydrogen molecule and applied the usual second-order perturbation method. Steensholt used the variational method with the Wang eigenfunction in the one-parameter form as given above. However, he took Wang's effective nuclear charge $Z_{\text{eff}} = 1.166$, while we considered

TABLE I. Polarizabilities in 10^{-25} cm^3 .

	α_{\perp}	α_{\parallel}	$\bar{\alpha}$	$ \alpha_{\parallel} - \alpha_{\perp} $	$\partial \alpha_{\perp} / \partial R$	$\partial \alpha_{\parallel} / \partial R$
Rosen eigenfunc. 2 parameters	7.4	7.5	7.4	0.1	$9.5 \times 10^{-17} \text{ cm}^2$	$11.0 \times 10^{-17} \text{ cm}^2$
Rosen eigenfunc. 1 parameter	6.7	7.1	6.9	.4	8.0	10.8
Wang eigenfunc. 2 parameters	7.3	7.5	7.3	.2	9.8	10.2
Wang eigenfunc. 1 parameter	6.6	7.1	6.8	.5	8.9	10.2
Steensholt using Wang eigenfunc. and 1 parameter	5.2	7.7	6.0	2.5		
Mrowka	8.5	6.1	7.7	2.4		
Experimental			8.0	3.6		

¹ G. Steensholt, *Zeits. f. Physik* **93**, 620 (1935); **94**, 770 (1935).

² E. Hylleraas, *Zeits. f. Physik* **65**, 209 (1930).

³ Hassé, *Proc. Camb. Phil. Soc.* **26**, 542 (1930); **27**, 66 (1931).

⁴ N. Rosen, *Phys. Rev.* **38**, 2099 (1931).

⁵ S. Wang, *Phys. Rev.* **31**, 579 (1928).

⁶ B. Mrowka, *Zeits. f. Physik* **76**, 300 (1932).