

**351.** *The Oxidation of Hydrocarbons and Their Derivatives. Part I. The Observation of the Progress of the Reaction by Pressure Change and by Analysis.*

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The kinetics of the oxidation in the gas phase of four esters (methyl formate, methyl acetate, methyl propionate, and ethyl formate) have been studied. The progress of the reaction was followed (*a*) by observation of pressure change, (*b*) by analytical measurement (mass spectrometric) of the rates of consumption of ester and of oxygen and the rates of formation of major products. The results show that the pressure-change measurements give a close indication of the progress of the reaction over its whole course.

THE kinetics of the oxidation of gaseous hydrocarbons and their derivatives are very complex and can only be elucidated by detailed study of the effect of many variables. For this a rapid and convenient method of measuring the reaction rate is absolutely essential. Laborious methods which restrict the numbers of observations are likely to cause important facts to be overlooked. The most commonly used technique has been to follow the course of the reaction by observation of the concomitant pressure change ( $\Delta p$ ). There is much indirect evidence that this method provides a substantially correct measure of the rate. The risk of error, however, is obvious from a simple example. The reaction  $C_2H_6 + 2\frac{1}{2}O_2 = 2CO + 3H_2O$  is attended by a pressure change ( $\Delta p$ ) equal to +1.5 times the initial ethane pressure. If the initial step were  $C_2H_6 + O_2 = C_2H_5 \cdot O_2H$  then the ratio for this would be -1. Since complex intermediates certainly do play an important rôle in the mechanism there is a real uncertainty.

In the present work analyses by mass spectrometer have been used to compare the pressure changes observed in the gas-phase oxidation of some esters with (*a*) the consumption of the ester and of oxygen, and (*b*) the formation of carbon monoxide and carbon dioxide.

## EXPERIMENTAL

Reactions took place in a silica vessel of about 250 c.c. capacity maintained at the required temperature in a thermostatically-controlled electric furnace. The reaction vessel was connected to a capillary mercury manometer, to storage vessels for reagents, and to the usual system of high-vacuum pumps. Provision was made for the withdrawal of the contents of the reaction vessel for analysis.

Analyses were made with a Metropolitan-Vickers mass spectrometer Type M.S.2 by conventional techniques. The admission of gas samples containing large proportions of oxygen to the ionisation chamber of a mass spectrometer leads to the more or less rapid reversal of the effects of the "conditioning" of the filament (a process for which the usual butene pre-treatment was used) with consequent deterioration in instrument stability. At the same time the mass spectra develop considerable spurious and variable contributions to the peak at  $m/e$  28. These must arise through reaction of the oxygen with carbonaceous deposits either on the filament or in the ionisation chamber. By increasing the butene pressure at which the pre-treatment was

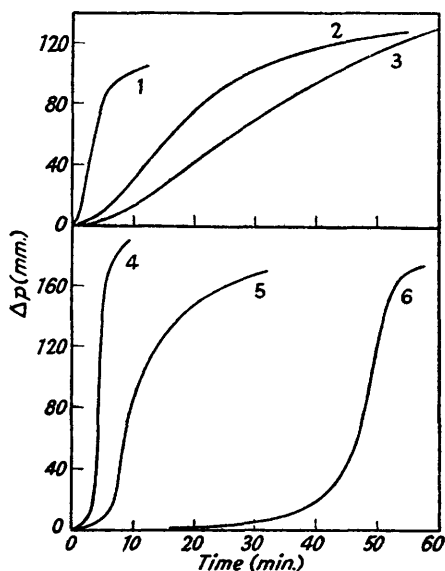


FIG. 1.  $\Delta p$ -time curves for the oxidation of esters.

1, Propyl formate.                   4, Methyl butyrate.  
2, Methyl formate.               5, Ethyl formate.  
3, Methyl acetate.               6, Methyl propionate.  
Temperature: Curve 1, 260°; curves 2—6, 380°.

carried out it was found possible to attain a state where these contributions to  $m/e$  28 became reproducible and proportional to the oxygen pressure, so that reliable corrections could be made. The overall stability of the instrument then remained constant for sufficiently long to allow the analysis of five or six gas samples. The butene treatment then had to be repeated.

Water is a major product of the reaction and some of that formed may be lost by condensation. In the majority of experiments, therefore, all water vapour was removed with phosphoric anhydride from the samples before analysis. An accurately measured amount of helium was always added to the ester-oxygen mixture in the reaction vessel as a reference gas so that the partial pressures of reactants and products in the vessel at the moment of sampling could be calculated from the analytical results, irrespective of any removal of water vapour.

Experiments were made with methyl formate, methyl acetate, methyl propionate, and ethyl formate. The esters were dried ( $\text{Na}_2\text{CO}_3$ ) and redistilled from phosphoric anhydride—a procedure which removes any unchanged alcohol or acid.<sup>1</sup> The accuracy of the analytical method was repeatedly checked by the analysis of synthetic mixtures containing known partial pressures of ester, oxygen, carbon monoxide, and carbon dioxide.

*Results.*—With each ester preliminary experiments were made to establish the form of the  $\Delta p$ -time curve. Series of successive experiments were then made in which gas samples for analysis were taken at representative points over the whole course of the reaction. As will appear in Part II,<sup>2</sup> ethyl formate differs from the other three esters in that its temperature-oxidation rate curve is of abnormal form, showing a maximum and a minimum. For this ester,

<sup>1</sup> Timmermans, "Physicochemical Constants of Pure Organic Compounds," Elsevier, 1950.

<sup>2</sup> Following paper.

therefore, analyses of products were made at a series of temperatures in the range 280—425°. With the other esters analyses were made at a single temperature.

The mass-spectra of the products of oxidation, with the exception of those from methyl propionate, did not show any sign of residual peaks which could be attributed to complex

FIG. 2. Rates of consumption of ester and oxygen and rates of formation of products as function of overall pressure change.

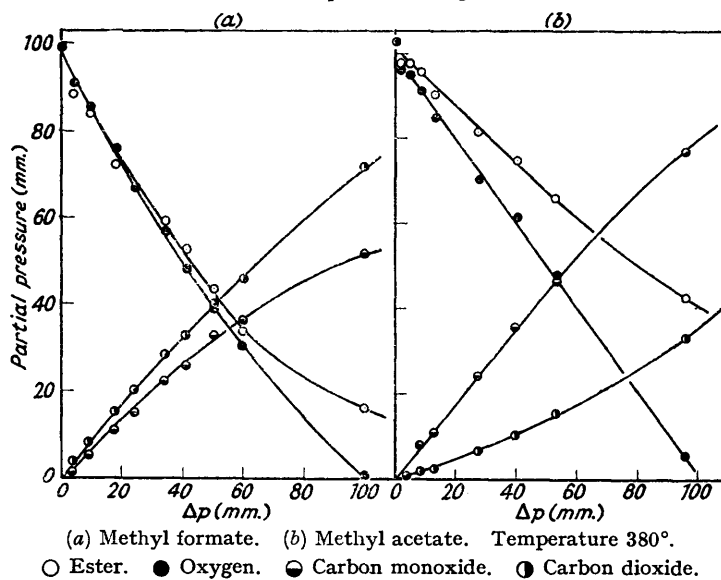
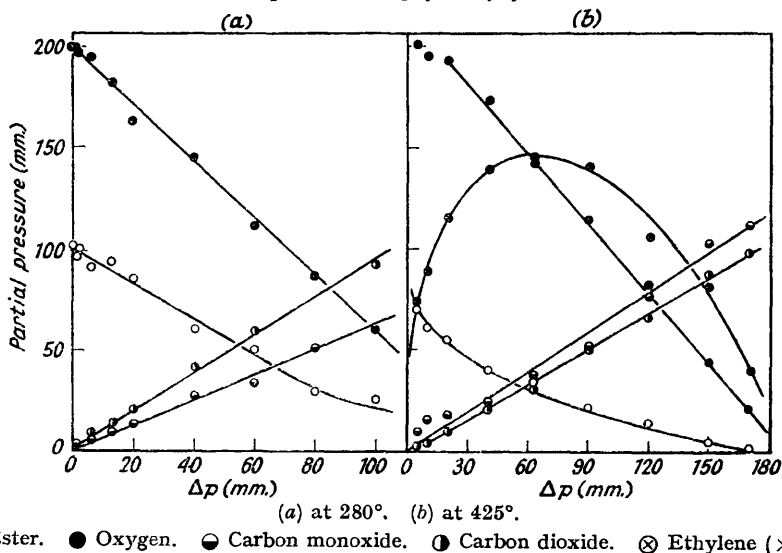


FIG. 3. Rates of consumption of ester and oxygen and rates of formation of products as function of overall pressure change for ethyl formate.



intermediates. This was to be expected, as such compounds would be liable to condense on the walls of the sample vessel or be removed by the drying agent. The mass spectra of the reaction products from the oxidation of methyl propionate, however, showed small residual peaks at  $m/e$  31: this peak is prominent in the mass-spectra of a number of oxygen-containing organic compounds, particularly alcohols and ethers.

Fig. 1 shows the form of the  $\Delta p$ -time curves for the oxidation of the esters for which analytical measurements were made, together with those for methyl butyrate and propyl formate for comparison. Fig. 2 shows the rates of consumption of ester and of oxygen, and the rates of formation of carbon monoxide and carbon dioxide plotted against  $\Delta p$  for methyl formate and methyl acetate. Fig. 3 gives the corresponding results for methyl propionate and Fig. 4 those for ethyl formate at the two extremes of the temperature range.

The ratio of carbon monoxide to carbon dioxide varies from ester to ester, and one effect of temperature is to alter the relative proportions of carbon monoxide and carbon dioxide formed. The Table gives, for future reference, the ratio of carbon monoxide to carbon dioxide for the four esters at 380°, and for the ethyl formate as a function of temperature.

*Ratio of carbon monoxide to carbon dioxide formed during oxidation of esters.*

Ester	Temperature 380°		Ethyl formate		Ethyl formate	
	CO/CO <sub>2</sub>		Temp.	CO/CO <sub>2</sub>	Temp.	CO/CO <sub>2</sub>
Methyl formate .....	0.77		280°	0.58	380°	1.0
Ethyl formate .....	1.0		310	0.67	390	1.0
Methyl propionate .....	2.0		340	0.73	425	1.1
Methyl acetate .....	3.5		360	0.90		

The analytical results show that there is a close linear relationship between the total pressure change on the one hand, and on the other, the rate of consumption of oxygen and the rates of

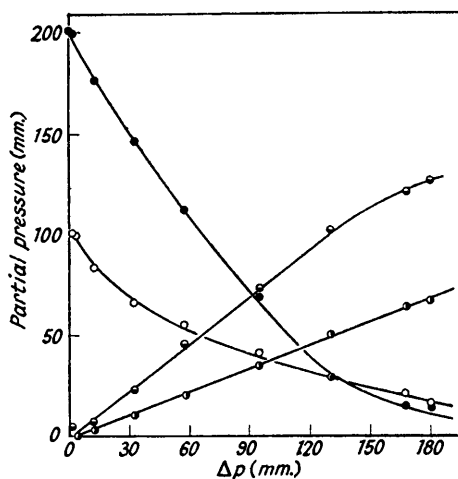


FIG. 4. Rates of consumption of ester and oxygen and rates of formation of products as functions of overall pressure change for methyl propionate at 380°.

○ Ester.                      ● Carbon monoxide.  
● Oxygen.                    ● Carbon dioxide.

formation of the final products, carbon monoxide and carbon dioxide. This relationship holds in spite of the fact that the pressure-time relationships follow the extremely sigmoid courses portrayed in Fig. 1. The measurements of the rates of disappearance of the esters themselves are the least reliable of the analytical data, depending in the early stages on relatively small differences in large quantities and being also liable to error through loss of ester by absorption in tap-grease or on the drying agent used to remove water vapour. Nevertheless, the analytical results for the rates of consumption of methyl formate and methyl acetate and of ethyl formate at the lower temperatures show a closely linear relation to  $\Delta p$ . The results for ethyl formate at higher temperatures show somewhat greater rates in the early stages than those corresponding to exact proportionality, but it is known that pyrolysis sets in here to an appreciable extent. (The amount of ethylene formed by pyrolysis was also estimated by mass spectrometer and is shown in Fig. 3.) A similar divergence from a linear relation with  $\Delta p$  is also shown by the rate of consumption of methyl propionate. With this ester, however, the induction period is particularly long (Fig. 1) and, as mentioned above, signs of complex intermediates can be seen in the mass spectra, suggesting that particularly large amounts must have been formed.

Taken as a whole the results obtained show that, except under the most extreme conditions, the rate of pressure change is a reliable measure of the true rate of oxidation.