112. *The Kinetics of the Oxidation of Ethylene by Nitrogen Dioxide.*

By T. L. Cottrell and T. E. Graham.

The reaction between nitrogen dioxide and ethylene has been studied by the static method, the total pressure and the nitrogen dioxide concentration being followed for initial pressures of between 3 and 12 cm. Hg of the reactants. The pressure at high temperatures rises rapidly, whereas at low temperatures there is a pressure drop followed by a rise. The NO_2 concentration decreases monotonically throughout the reaction. Rates of reaction were measured by drawing tangents to the curves of $[NO_2]$ against time.

The results were systematised by considering the initial slope of the $[NO_2]$–time curve:

$$-(\mathrm{d}[NO_2]/\mathrm{d}t)_{t=0} = k_{\mathrm{III}}[NO_2]^{1\cdot 8}[C_2H_4]^{1\cdot 2}$$

A plot of $\log_{10} k_{\mathrm{III}}$ against $1/T$ gave two intersecting straight lines with equations:

$$k_{\mathrm{III}} = 10^{8\cdot 5} \exp(-12{,}500/\boldsymbol{R}T)\ \mathrm{l.}^2\ \mathrm{mole}^{-2}\ \mathrm{sec.}^{-1}\ (160\text{—}220^\circ),$$
$$k_{\mathrm{III}} = 10^{10\cdot 9} \exp(-18{,}000/\boldsymbol{R}T)\ \mathrm{l.}^2\ \mathrm{mole}^{-2}\ \mathrm{sec.}^{-1}\ (220\text{—}280^\circ).$$

The $[NO_2]$–t curve in the course of a run was approximately of first order, more nitrogen dioxide having disappeared at a given time than would be expected from the third-order law, presumably because it reacts further with a product of the initial reaction. The process governing the rate of pressure rise had an activation energy of 17,000 cal.

The gaseous products were almost entirely carbon dioxide, carbon monoxide, and nitric oxide. The other products included an oil and a small amount of carbon-like material. Addition of nitric oxide or of air had no effect on the kinetics of disappearance of nitrogen dioxide. Increasing the surface : volume ratio by a factor of 8 had no effect at high temperature, and only a slight effect at low temperatures.

These facts are consistent with the view that nitrogen dioxide adds on to ethylene in the molecular ratio of 2 : 1, and that this product decomposes to give fragments capable of reacting with further nitrogen dioxide with complete oxidation.

In the combustion of organic nitrates, nitrogen dioxide is considered to be split off and to oxidise the other fragments (Phillips, *Nature*, 1947, **160**, 753; 1950, **165**, 564). Thus oxidation of organic compounds by nitrogen dioxide may be important in the chemistry of the propagation of reaction in nitrates. The oxidation of formaldehyde (Pollard and Wyatt, *Trans. Faraday Soc.*, 1949, **45**, 760, 767) has therefore already been studied.

Acetaldehyde (McDowell and Thomas, *ibid.*, 1950, **46**, 1030) and acetylene (Thomas, personal communication) have also been studied, although for other reasons. It was of interest to examine the oxidation of ethylene, as a representative olefin and because it has been suggested that ethylene formed by the unimolecular decomposition of nitroethane would be readily oxidised by nitrogen dioxide produced from the nitrous acid left after the initial stage of the decomposition (Cottrell, Graham, and Reid, *ibid.*, 1951, **47**, 1089).

EXPERIMENTAL

Materials.—Nitrogen dioxide, prepared by heating mixed lead nitrate and sand over which dry oxygen was flowing, was distilled several times over phosphoric oxide and stored at liquid-nitrogen temperature. Commercial ethylene was passed over phosphoric oxide and potassium hydroxide and distilled several times.

Apparatus.—The " Pyrex " reaction vessel of volume 500 cm.^{3} was heated in a vertical electrical furnace, controlled to ±0·1° by a " Sunvic " resistance thermometer controller. Temperature measurement was by calibrated chromel–alumel thermocouple. A glass spiral manometer (Yorke, *J. Sci. Instr.*, 1945, **22**, 196; 1948, **25**, 16), attached to the vessel by heated capillary tubing, was enclosed in a heated oil-bath. Pressures were read to ±0·02 cm. of Hg, by use of a light source, mirror on the gauge, and scale. The furnace had windows through which a light beam was passed on to a photo-cell, whose output was balanced in a bridge circuit. The bridge reading was calibrated against the nitrogen dioxide concentration (McDowell and Thomas, *loc. cit.*).

The system was evacuated by a mercury diffusion pump. Nitrogen dioxide was admitted to the reaction vessel, the pressure and bridge reading being noted (thus checking the calibration of the photo-cell bridge circuit). Ethylene was then admitted during about 5 seconds and the reaction followed by noting the pressure and bridge reading. The products could be removed and admitted to a trap cooled in liquid nitrogen, which could warm to −80°, and the permanent gases could then be removed by a Töpler pump, either to a cell for infra-red spectroscopic examination or to a gas sampler for chemical analysis in a Bone and Wheeler apparatus.

Kinetic Results.—At 290° the kinetic results were not very reproducible, and at pressures of over 30 cm. explosions occurred. It was established in these runs that the pressure increase is proportional to the initial pressure of nitrogen dioxide, and is equal to $0{\cdot}45[NO_2]_{t=0}$, ethylene being present in excess. A few of the later runs at lower temperatures were continued sufficiently to check this. They agreed, except at the lowest temperatures where the pressure increase was less. Details of selected runs are given in Tables 1—3. In Table 1 are given the

TABLE 1. *Ethylene–nitrogen dioxide reaction. Details of selected runs.*

Run	Temp.	p-NO_2, cm.	p-C_2H_4, cm.	$(d[NO_2]/dt)_{t=0}$, cm./min.	k_{III}, cm.$^{-2}$ min.$^{-1}$	k_L, sec.$^{-1}$	Remarks
94	279·5°	5·87	5·68	8·0	$4{\cdot}1 \times 10^{-2}$	$5{\cdot}3 \times 10^{-3}$	
107	,,	5·98	2·12	3·4	4·5	4·8	
113	,,	5·86	10·56	14·2	3·9	5·4	
132	,,	1·96	5·88	0·95	4·2	—	
138	,,	7·96	5·99	16·0	4·2	5·5	
150	269·0	6·20	5·80	5·9	$2{\cdot}6_8 \times 10^{-2}$	$3{\cdot}2 \times 10^{-3}$	
151	,,	6·00	2·85	$2{\cdot}3_4$	$2{\cdot}6_6$	3·0	
153	,,	6·30	9·10	9·5	$2{\cdot}4_4$	$3{\cdot}1_5$	
172	,,	4·55	6·15	$3{\cdot}1_5$	$2{\cdot}3_4$	—	6·05 cm. of NO added
178	,,	3·31	11·89	4·0	$2{\cdot}3_9$	—	
179	,,	11·08	3·17	7·5	$2{\cdot}4_9$	—	
181	258·3	5·94	6·15	$4{\cdot}5_0$	$2{\cdot}0_6 \times 10^{-2}$	$2{\cdot}2_7 \times 10^{-3}$	
186	247·8	6·12	6·10	3·6	$1{\cdot}5_8 \times 10^{-2}$	$1{\cdot}96 \times 10^{-3}$	
189	,,	11·45	3·75	6·3	$1{\cdot}6_1$	$1{\cdot}7_7$	
193	,,	3·95	8·05	2·20	$1{\cdot}5_2$	$1{\cdot}8_8$	
197	233·9	6·25	6·22	$2{\cdot}2_5$	$9{\cdot}3 \times 10^{-3}$	—	
203	218·5	6·05	5·90	$1{\cdot}1_9$	$5{\cdot}5 \times 10^{-3}$	$6{\cdot}1 \times 10^{-4}$	
210	205·1	5·95	5·95	0·90	$4{\cdot}3 \times 10^{-3}$	$4{\cdot}3 \times 10^{-4}$	
212	,,	12·03	2·98	1·34	$4{\cdot}1_2$	2·8	
216	190·8	5·92	5·69	0·64	$3{\cdot}2 \times 10^{-3}$	—	
229	164·8	5·95	6·12	0·35	$1{\cdot}6_1 \times 10^{-3}$	—	
235	,,	20·05	9·90	$5{\cdot}3_8$	$1{\cdot}5_6$	—	
240	270·8	7·00	7·00	$8{\cdot}3_5$	$2{\cdot}4_8 \times 10^{-2}$	—	Packed reaction vessel
241	191·5	6·25	7·60	$1{\cdot}2_5$	$4{\cdot}0_5 \times 10^{-3}$	—	,, ,,
243	271·3	6·21	6·45	6·4	$2{\cdot}5_5 \times 10^{-2}$	—	Packed vessel, 6·20 cm. of air added

TABLE 2. *Ethylene–nitrogen dioxide reaction. Pressure–time data.*

Run	Δ*p* (cm. Hg) at *t* (min.)													
t =	0	¼	½	¾	1	1½	2	3	4	6	8	10	20	
94	0·00	0·16	0·28	0·41	0·59	0·84	1·02	1·37	1·59	1·70	—	—	—	—
107	0·00	0·09	0·14	0·29	0·39	0·60	0·82	1·10	1·38	1·70	1·94	2·10	2·58	—
113	0·00	0·06	0·18	0·35	0·46	0·67	0·85	1·12	1·33	1·60	—	—	—	—
132	0·00	0·02	0·02	0·03	0·04	0·12	0·15	0·22	0·30	—	—	—	—	—
138	0·00	0·22	0·45	0·62	0·81	1·09	1·31	1·69	1·93	—	—	—	—	—
150	0·00	0·00	0·02	0·10	0·20	0·41	0·60	0·86	1·09	1·39	1·59	1·78	—	—
151	0·00	0·00	0·05	0·14	0·21	0·34	0·54	0·75	0·96	1·26	1·50	1·70	—	—
153	0·00	0·00	0·08	0·18	0·29	0·46	0·60	0·89	1·10	1·43	1·65	—	—	—
172	0·00	0·00	0·00	0·00	0·04	0·13	0·23	0·44	0·64	—	—	—	—	—
178	0·00	0·01	0·01	0·02	—	0·14	0·20	0·34	0·40	—	—	—	—	—
179	0·00	0·20	0·35	0·56	0·75	1·08	1·29	1·81	2·20	—	—	—	—	—
181	0·00	0·02	0·04	0·05	0·12	0·26	0·39	0·56	0·77	1·05	1·28	1·45	—	—
t =	0	½	1	1½	2	2½	3	4	5	6	8	10	20	60
186	0·00	0·00	0·05	0·11	0·22	0·31	0·40	0·59	0·71	0·86	1·06	1·26	—	—
189	0·00	−0·10	+0·01	0·19	0·39	0·55	0·70	0·99	1·25	1·51	1·92	2·29	—	—
193	0·00	−0·09	−0·09	−0·05	0·00	0·05	0·10	0·20	0·28	0·37	0·52	0·62	—	—
197	0·00	−0·21	−0·27	−0·30	−0·24	−0·21	−0·12	−0·02	0·09	0·23	0·42	0·58	1·22	2·15
t =	0	1	2	4	6	8	10	15	20	25	30	40	50	60
203	0·00	−0·38	−0·54	−0·53	−0·37	−0·23	−0·05	0·30	0·59	0·84	1·00	1·31	1·54	1·66
t =	0	1	2	4	7	10	15	20	30	40	60	80	100	120
210	0·00	−0·35	−0·59	−0·77	−0·80	−0·72	−0·48	−0·25	0·15	0·44	0·85	1·13	—	—
212	0·00	−0·49	−0·72	−0·91	−0·88	−0·69	−0·31	0·07	0·69	1·22	2·03	2·64	3·11	3·50
216	0·00	−0·31	−0·54	−0·88	−1·11	−1·21	−1·19	−1·11	−0·92	−0·50	−0·33	−0·07	0·15	—
229	0·00	−0·20	−0·39	−0·72	−1·10	−1·39	−1·67	−1·87	−2·05	−2·09	—	—	—	—
235	0·00	−2·45	−4·00	−5·45	−5·80	−5·31	−4·12	−3·06	−1·42	−0·46	+0·77	1·60	2·19	—
t =	0	¼	½	¾	1	1½	2	3	4	6	8	10	20	30
240	0·00	0·10	0·35	0·60	0·90	1·38	1·70	2·15	2·42	2·77	—	—	—	
241	0·00	—	−0·27	—	−0·42	−0·60	−0·70	−0·88	−0·93	−1·00	−1·00	—	−0·60	−0·26
243	0·00	0·05	0·22	0·41	0·60	0·88	1·12	1·36	—	—	—	—	—	—

TABLE 3. *Ethylene–nitrogen dioxide reaction.* [NO$_2$]–*t data.*

Run	[NO$_2$], cm., at *t* (min.)													
t =	0	¼	½	¾	1	1¼	1½	1¾	2	2½	3	3½	4	5
94	5·8$_5$	4·3$_0$	3·0$_2$	2·2$_3$	1·6$_0$	—	1·2$_0$	—	0·9$_0$	—	—	—	—	—
107	6·0$_0$	5·4$_0$	4·6$_0$	4·1	3·8	3·3	3·0	2·8	2·6	—	—	—	—	—
113	5·8	3·2	1·8	1·2	0·8	0·7	—	—	—	—	—	—	—	—
132	1·9$_5$	1·7$_2$	1·4$_9$	1·3$_0$	1·1$_0$	0·9$_5$	0·8$_5$	0·7$_0$	0·5$_5$	—	—	—	—	—
138	8·0	4·9	3·1$_5$	2·3$_0$	1·8	1·5	—	—	—	—	—	—	—	—
150	6·2	5·0	3·9	3·1	2·4	2·1	1·7	1·4	1·3	—	—	—	—	—
151	6·0	5·5	5·1	4·6$_5$	4·1$_5$	3·7	3·4	3·1	2·8	—	—	—	—	—
153	6·3	4·5	2·9	2·1$_5$	1·5$_5$	1·1	—	—	—	—	—	—	—	—
172	4·6	3·9	3·2	2·8	2·2$_5$	1·9	1·6$_5$	1·4$_5$	1·3	—	—	—	—	—
178	3·3	2·4	1·7$_5$	1·3	1·0	0·8	0·6$_5$	0·5$_5$	0·4$_5$	—	—	—	—	—
179	11·1	10·0$_5$	8·3	7·2	6·3	5·6	5·1	4·6	4·3$_5$	3·8$_5$	3·5	—	—	—
181	6·0	5·6$_5$	4·1$_5$	3·4	2·8	2·4	2·0	1·6$_5$	1·4$_5$	1·1$_5$	1·0	—	—	—
186	6·1	5·3	4·6	3·9	3·3$_5$	2·8$_5$	2·4$_5$	2·1$_5$	1·8$_5$	1·4$_5$	1·2	—	—	—
189	11·5	10·3	9·1	8·0	7·1$_5$	6·5	5·8$_5$	5·4$_5$	5·0$_5$	4·4	4·0	—	—	—
193	3·9$_5$	3·4	2·9	2·5$_5$	2·2	1·9$_5$	1·6	1·4	1·2$_5$	0·9$_5$	—	—	—	—
197	6·3	6·0$_5$	5·6	5·1	4·6	4·1$_5$	3·9	3·4$_5$	3·1$_5$	2·7	2·3	2·0$_5$	1·7$_5$	—
203	6·1	5·9	5·6	5·3$_5$	5·1	4·8$_5$	4·6	4·3$_5$	4·1	3·7	3·3	3·0$_5$	2·8	2·3
t =	0	½	1	1½	2	2½	3	3½	4	4½	5	6	8	10
210	6·0	5·6	5·3	4·9	4·6	4·2	3·9	3·7	3·4	3·2	3·0	2·7	2·2	—
212	12·0	11·5	10·9	10·3$_5$	9·9$_5$	9·5	9·1	8·8	8·4$_5$	8·0$_5$	7·8$_5$	7·3$_5$	6·6$_5$	6·1
216	5·9	5·6	5·3	5·0	4·8	4·5	4·3$_5$	4·2	4·0	3·8	3·6	3·4	2·9$_5$	2·5$_5$
229	5·9$_5$	5·8	5·6	5·4$_5$	5·3	5·2	5·1	5·0	4·9	4·7$_5$	4·6	4·3$_5$	4·0	3·6$_5$
235	20·0	17·7	15·9	14·6	13·5	12·4	11·6	11·1	10·5	9·9	9·5	8·8	7·7	6·9
t =	0	¼	½	¾	1	1¼	1½	1¾	2	2½	3	3½	4	
240	7·0	5·3	3·9	2·8	2·3	1·8	1·6	1·3	1·1	—	—	—	—	—
241	6·3	—	5·7	—	5·2	—	4·9	—	4·5	4·2	3·9	3·7	3·5	—
243	6·2	4·8	3·7	2·9	2·5	2·0	1·7	1·5	1·4	—	—	—	—	—

temperature, the initial pressures of reactants, the initial slope of the $[NO_2]$–time curve, a third-order constant, and a first-order constant. In Table 2 are given the pressure–time data, and in Table 3 the $[NO_2]$–time data. At 279·5° the $[NO_2]$–time curves are not very satisfactory, because the reaction is too fast to follow accurately. The runs are numbered in chronological order. The results show that, although at higher temperatures the pressure increases with time, yet at lower temperatures there is a decrease followed by a rise. The NO_2 concentration decreases monotonically throughout the reaction. Typical runs are shown in Fig. 1. The pressure change is not simply related to the amount of NO_2 reacting, and thus the pressure–time curves may not be susceptible of a straightforward kinetic interpretation.

Apparently two reactions, addition of nitrogen dioxide (with pressure decrease) and oxidation (with pressure increase) are proceeding, either in series or in parallel, with different activation energies. Attempts at kinetic analysis were largely confined to the $[NO_2]$–time curves. Runs at 269° were first considered. The initial slope of the $[NO_2]$–time curve was obtained by plotting the readings, drawing tangents at various pressures of NO_2, and extrapolating back to the known original pressure. The initial slope depended on $[NO_2]^{1\cdot 8}$ and $[C_2H_4]^{1\cdot 2}$. The results at 279·5°, however, seemed to be better expressed by the simple powers 2 and 1. The non-integral powers may be due to a side reaction which is less important at high temperature.

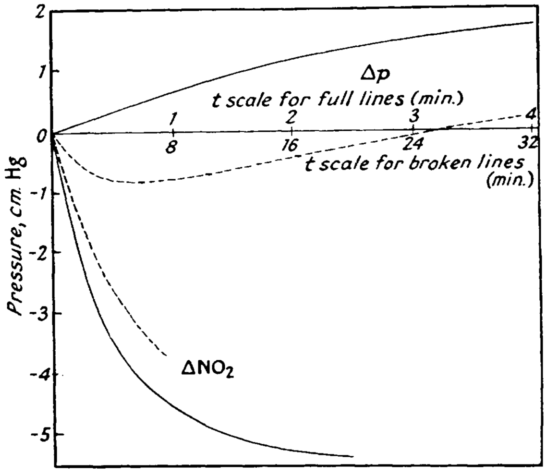


FIG. 1. *p–t and* $[NO_2]$*–t plots for run* 106 ———, *and run* 210 – – – –.

In Table 1 are given the constants obtained at all temperatures, it being assumed that $(-d[NO_2]/dt)_{t=0} = k_{III}[NO_2]^{1\cdot 8}[C_2H_4]^{1\cdot 2}$, except for 279·5°, where the powers 2 and 1 are used. The constancy of k_{III} for changes by a factor of 3 or 4 in the pressures of the reactants is good; clearly, the initial step is kinetically the same throughout the temperature range. This implies that the addition and oxidation reactions must take place in series.

A plot of $\log_{10} k_{III}$ against $1/T$ for all runs falls into two straight-line segments, which have the equations given on p. 556.

The slope of the $[NO_2]$–t curve was approximately proportional to the pressure of NO_2 during a run up to about 50% reaction, *i.e.*, $-d[NO_2]/dt = k'[NO_2]_t$, although of course k' depended on the initial pressures of NO_2 and ethylene. This apparent first-order rate of disappearance of NO_2 was checked by calculating first-order constants by using the integrated form of the first-order law. The " constants " decreased slightly as the reaction proceeded, except at the lowest temperatures, when the decrease was rapid. The approximation was less good for high and for low initial concentration of NO_2.

The vessel was packed with Pyrex capillary tubing to give an increase in the surface : volume ratio by a factor of 8. At high temperatures k_{III} was unchanged; at low temperatures it was increased by about 30%, showing that the surface effect is slight. Addition of NO (runs 170—172) and air (run 243) had little effect on k_{III}.

Although a simple molecular interpretation of the pressure–time curves was not expected, the part involving pressure increase was roughly of first order, as determined by Guggenheim's method (*Phil. Mag.*, 1926, **2**, 538). At high temperatures the maximum slope of the pressure–time curve was roughly proportional to the initial pressure of NO_2 only. In all these runs, the ethylene was present in excess, so that the amount of an intermediate formed might be expected to be proportional to the initial pressure of NO_2. The first-order constants obtained from the pressure increase are given in Table 1 as k_I. The temperature dependence of k_I is given by $k_I = 10^{4.35}e^{-17,000/RT}$ sec.$^{-1}$. For those runs in which the NO_2/C_2H_4 ratio is large, k_I is smaller than usual. These results were not included in the activation-energy plot.

Whereas the addition of NO had no effect on the $[NO_2]$–t curves, yet it had a marked effect on the pressure–time curve, causing an apparent induction period before the pressure started to increase.

Stoicheiometry and Analyses.—Where there was no initial pressure drop the total pressure increase of 45% of the initial pressure of NO_2 may be compared with a 50% pressure increase calculated for $6NO_2 + C_2H_4 \longrightarrow 2CO_2 + 2H_2O + 6NO$. As mentioned above, the pressure increase is not simply related to the change in NO_2 pressure. In the runs at low temperature, where there is an initial pressure decrease, the ratio of the initial slope of the $[NO_2]$–t curve to the initial slope of the pressure–time curve was noted (Table 4). At temperatures immediately above those for which results are given in the Table, the pressure decrease was too rapid to be measured accurately, and at even higher temperatures it was not observed. The ratio is greater the higher the temperature. There are only a few possible addition compounds, so the number of simple equations which can be written to explain the pressure drop is small. Three which give products for which there is evidence at lower temperatures (cf. Levy, Scaife, and Smith, *J.*, 1946, 1096) are

TABLE 4. *Ratio of* $(d[NO_2]/dt)_{t=0}$ *to* $(dp/dt)_{t=0}$ *for various runs.*

Run	Temp.	Ratio	Mean	Run	Temp.	Ratio	Mean
203	218·5°	2·4	2·60	210	205·1°	2·0	2·03
204	,,	2·6		211	,,	2·0	
207	,,	2·6		212	,,	2·0	
208	,,	2·5		213	,,	2·1	
209	,,	2·9		214	,,	2·1	
229	164·75	1·8	1·72	215	,,	2·0	
230	,,	1·8		216	190·75	2·1	1·93
233	,,	1·7		218	,,	1·9	
235	,,	1·6		221	,,	1·8	

$$2NO_2 + C_2H_4 \longrightarrow C_2H_3{\cdot}NO_2 + \tfrac{1}{2}(H_2O + NO + NO_2) \qquad \Delta[NO_2]/\Delta p = 3$$
$$2NO_2 + C_2H_4 \longrightarrow C_2H_3{\cdot}NO_2 + HNO_2 \qquad \Delta[NO_2]/\Delta p = 2$$
$$2NO_2 + C_2H_4 \longrightarrow C_2H_4(NO_2)_2 \qquad \Delta[NO_2]/\Delta p = 1$$

Presumably formation of nitroethylene is favoured at higher temperatures, whereas formation of dinitroethane (the structure being unspecified for the present) is favoured at lower temperatures.

Direct interpretation of these p–t results in terms of such equations is not quantitatively possible because of side reactions. Polymerisation of nitroethylene might well take place, causing a smaller value of $\Delta[NO_2]/\Delta p$, and in addition the results of gas analyses show that some complete oxidation has taken place even at very short times, which would cause a larger value of $\Delta[NO_2]/\Delta p$ than expected.

Qualitative analysis by infra-red spectroscopy of the gaseous products showed carbon dioxide, carbon monoxide, nitric oxide, and unchanged ethylene. Particularly at the lower temperatures, the products when removed for analysis contained a high-boiling oil, which was not analysed, but was thought to be a mixture of nitroethylene, dinitroethane, and possibly nitroethyl nitrite. A deposit of dark material was gradually formed in the tubes leading to the reaction vessel. The gaseous products were analysed in the Bone and Wheeler apparatus for carbon dioxide, nitric oxide, ethylene, and carbon monoxide, potassium hydroxide, ferrous sulphate, silver sulphate and concentrated sulphuric acid, and ammoniacal cuprous chloride being used as absorbents. The residue was generally 2—3% and never more than 5%. There is some interaction between these reagents, and at the times of greatest interest, near the beginning of the reaction, the samples were small, so that the results were not very reproducible. Accordingly, only a few analyses were carried out, all for runs at 190·6°, with 10 cm. of NO_2 and 5 cm. of C_2H_4. After short times (1—2 minutes) the permanent gas contained carbon dioxide and carbon monoxide in the ratio of about 5 : 1, nitric oxide roughly equivalent to the oxides of carbon, and unchanged ethylene. The NO analyses were particularly variable because of the possibility of carrying a small amount of NO_2 over into the Töpler pump, where it would react to give NO. Typical results for the composition of the permanent gas are given in Table 5 :

TABLE 5. *Typical compositions of permanent-gas products from reaction of* 10 *cm. of* NO_2 *and* 5 *cm. of* C_2H_4 *at* 190·6°.

Time stopped	CO_2, %	NO, %	C_2H_4, %	CO, %
1½ min.	4·5	14·1	75·0	1·0
1½ min.	4·0	19·5	73·4	0·9
2 min.	5·4	14·5	74·0	1·1

the residue was not analysed, and probably consisted of nitrogen with possibly a little nitrous oxide. No attempt was made to refine the method of analysis because products are likely to be too complex.

DISCUSSION

The results suggest that 2 mols. of nitrogen dioxide are added to one of ethylene, a process which can take place in two different ways with activation energies of approximately 18 and 12·5 kcal. to give an addition product which decomposes, possibly with nitroethylene as an intermediate, to fragments which are completely oxidised by more nitrogen dioxide. The process controlling the oxidation has an activation energy of about 17 kcal.

In discussing the initial rate of reaction of NO_2, it will be assumed that the main process is of the second order in NO_2 and the first order in ethylene, although the exact figures are 1·8 and 1·2. Two mechanisms for an apparent third-order reaction suggest themselves, as follows :

$$\begin{array}{lllr}
\text{Scheme I} & NO_2 + C_2H_4 & \longrightarrow NO_2{\cdot}C_2H_4 \quad . \; . \; . \; . \; . \; . \; . \; . & (1) \\
 & NO_2{\cdot}C_2H_4 & \longrightarrow NO_2 + C_2H_4 \quad . \; . \; . \; . \; . \; . & (2) \\
 & NO_2 + NO_2{\cdot}C{\cdot}H_4 & \longrightarrow C_2H_4(NO_2)_2 \quad . \; . \; . \; . \; . \; . & (3) \\
\text{Scheme II} & NO_2 + NO_2 & \longrightarrow N_2O_4 \quad . \; . \; . \; . \; . \; . \; . \; . & (4) \\
 & N_2O_4 & \longrightarrow NO_2 + NO_2 \quad . \; . \; . \; . \; . \; . & (5) \\
 & N_2O_4 + C_2H_4 & \longrightarrow C_2H_4(NO_2)_2 \quad . \; . \; . \; . \; . \; . & (6)
\end{array}$$

Applying the usual stationary state assumption to $NO_2{\cdot}C_2H_4$, we find that Scheme I gives

$$-\,\mathrm{d}[NO_2]/\mathrm{d}t = 2k_1k_3[NO_2]^2[C_2H_4]/(k_2 + k_3[NO_2])$$

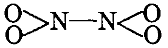
and applying it to N_2O_4, we find that Scheme II gives

$$-\,\mathrm{d}[NO_2]/\mathrm{d}t = 2k_4k_6[NO_2]^2[C_2H_4]/(k_5 + k_6[C_2H_4])$$

Hence, in each scheme if the second term in the denominator is small compared to the first, third-order kinetics are obtained. If the second term has an effect in Scheme I, the dependence on NO_2 might be slightly less than on the second power, whereas in Scheme II the ethylene dependence might be slightly less than the first power. Thus Scheme I is to be preferred on these grounds.

The experimental activation energy is 12·5 kcal. at low temperatures and 18·0 kcal. at higher temperatures. Scheme I gives the activation energy as $E_1 + E_3 - E_2$; E_2 and E_3 might be expected to be small, so that the overall activation energy is expected to be $\sim E_1$. The reaction (1) involves the formation of a C–N bond and the conversion of a C═C bond into a C–C bond. The bond energies given by Coates and Sutton (*J.*, 1948, 1187) being used, this reaction should be exothermic to the extent of about 10 kcal., so there is no energetic reason why E_1 should not be 12—18 kcal. Scheme II gives the activation energy as $E_4 + E_6 - E_5$; $E_4 - E_5$ is known to be about -13 kcal. (Richards and Reid, *J. Chem. Physics*, 1933, **1**, 114), so the overall activation energy, $E = E_6 - 13$ kcal. Thus E_6 must be 25—31 kcal. if Scheme II is correct. Reaction (6) is certainly exothermic, though this seems perhaps rather a high value for E_6.

The experimental frequency factors are $10^{8\cdot5}$ and $10^{10\cdot9}$ $l.^2$ $mole^{-2}$ $sec.^{-1}$. Scheme I makes the overall factor the product of two bimolecular factors divided by the unimolecular factor for reaction (2). If the factor for reactions (1) and (3) is equal to the collision frequency, then the numerator is 10^{20}—10^{24}, and the denominator 10^{12}—10^{14}. This allows the overall frequency factor to be between 10^6 and 10^{12}. The experimental values lie within this range, but surprisingly high in it; in many reactions involving NO_2 the bimolecular frequency factor is appreciably less than the collision number. This could be accounted for if the frequency factor for unimolecular radical decompositions were less than that usually found for molecules, and there is some evidence of this (cf. Howlett, *Trans. Faraday Soc.*, 1952, **48**, 25). Scheme II gives a similar result, but here the frequency factor of (5) is known to be at the high end of the range for unimolecular frequency factors (Richards and Reid, *loc. cit.*), and thus the overall factor is likely to be lower than that for Scheme I if it is assumed that all the bimolecular reactions have the same frequency factors. Since the experimental frequency factor is if anything rather high, this examination favours Scheme I.

A further support for Scheme I lies in the possibility of explaining the two activation energies of the reaction. The O–N–O molecule can form either a C–N bond or a C–O bond when adding to a carbon atom, and it is not to be expected that these two processes will have the same activation energies or frequency factors. That both modes of addition are possible has been shown by the Billingham workers who have obtained nitroethyl nitrate and dinitroethane from the reaction between nitrogen dioxide and ethylene (Levy, Scaife, and Smith, *loc. cit.*). It is also significant that in the reaction between nitrogen dioxide and formaldehyde, in which addition is also postulated, there are also two activation energies which might be explained similarly. On the other hand, if N_2O_4 is a symmetrical plane molecule of the formula  ${}^{O}_{O}\!>\!N{-}N\!<\!{}^{O}_{O}$ as is suggested by spectroscopic (cf. Herzberg, "Infra Red and Raman Spectra," New York, 1945) and *X*-ray (Broadley and Robertson, *Nature*, 1949, **164**, 915) evidence, then it is much less easy to see how addition could take place in two different ways. Also, it is not possible to see how N_2O_4 would add on to ethylene even in one way, except by breaking and forming several bonds in the one putatively elementary step.

The relation between the initial rates of disappearance of NO_2 and of pressure decrease shown in Table 4 points to the formation of nitroethylene, probably by decomposition of nitroethyl nitrite. The nitroethylene formation appears to be temperature-dependent and to become the main reaction by about 220°, the temperature at which there appears to be a break in the activation energy curve. To take this into account, reaction Scheme I would have to consist of reactions (1), (2), and (3) as before, with the addition of

$$NO_2 + NO_2{\cdot}C_2H_4 \longrightarrow C_2H_4(O{\cdot}NO)(NO_2) \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (3a)$$

$$C_2H_4(O{\cdot}NO)(NO_2) \longrightarrow C_2H_3{\cdot}NO_2 + \tfrac{1}{2}(H_2O + NO + NO_2) \quad . \ . \ . \ . \quad (7)$$

The compounds in parentheses are assumed to result from the decomposition of HNO_2.

This gives, with the obvious stationary-state assumptions,

$$\frac{-\,d[NO_2]}{dt} = \frac{k_1(2k_3 + k_{3a})[NO_2]^2[C_2H_4]}{k_2 + (k_3 + k_{3a})[NO_2]}$$

a relation of precisely the same form as before, and one which should lead to an activation energy plot with different slopes in the regions corresponding to the predominance of reaction (3) and of reaction (3*a*). With these activation energies not very different, a sharply segmented plot would not be expected, and the true activation energies and frequency factors would differ slightly from those deduced simply by drawing two straight lines through the experimental points. This consideration, which applies equally to the work of Pollard and Wyatt on formaldehyde (*loc. cit.*), makes only a slight difference to the numerical values and does not affect the argument.

Although the experimental results could probably be fitted to a smooth curve in the region of intersection of the straight lines actually drawn, in neither set is the precision sufficiently great to justify this procedure. Exactly similar kinetic results would follow if the mechanism of formation of nitroethylene involved hydrogen abstraction, as in (3*b*):

$$C_2H_4{\cdot}NO_2 + NO_2 \longrightarrow C_2H_3{\cdot}NO_2 + HNO_2 \quad . \ . \ . \ . \ . \ . \ . \quad (3b)$$

The subsequent apparent first-order decrease of NO_2 with time in any given run can be explained on the view that it is reacting further with fragments from the decomposition of the addition compounds. It is not possible to put forward a detailed scheme for this, as the number of possible intermediates is large, but that such a scheme could in principle explain the results was shown by the numerical solution * of the differential equations describing the reactions

$$2A + B \longrightarrow C \ (8); \quad A + C \longrightarrow D \ (9)$$

Here A and B are nitrogen dioxide and ethylene, and C may be a series of intermediates the last member of which reacts with nitrogen dioxide. In Fig. 2 are plotted the experimental results for the disappearance of NO_2 in run 203 (for example) and the theoretical curves corresponding to

$$-\,\mathrm{d}a/\mathrm{d}t = ka^2b \ \text{(3rd order)}$$

and

$$-\,\mathrm{d}a/\mathrm{d}t = ka_0b_0a \ \text{(1st order with same initial slope)}$$

Here concentrations are indicated by lower case letters, the subscript 0 referring to zero time. Also shown is the curve corresponding to the system of equations (8) and (9) with $\kappa = 6\ k_9/k_8b_0 = 80$.

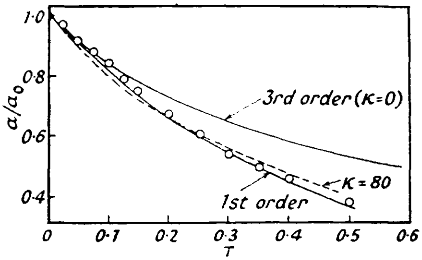


FIG. 2. *Showing apparent first-order decrease of* NO_2: o *experimental points for run* 203.

(The time scale is dimensionless, $\tau = k_8a_0b_0t$.) This curve fits the results fairly well. The rate constant for the second-order reaction (k_9) may be obtained from κ since k_8 (the third-order rate constant) is known from the initial slope; this gives a value for k_9 of approximately 10 l. mole^{-1} sec.$^{-1}$ which, if combined with an activation energy of 17,000 cal., gives a frequency factor of $10^{8\cdot5}$ l. mole^{-1} sec.$^{-1}$, a reasonable value for a second-order reaction frequency factor.

The " first-order rate constant " characterising the pressure rise cannot be interpreted on a molecular basis. The low frequency factor ($10^{4\cdot35}$ compared with 10^{13} for a unimolecular reaction) shows that the process is not a simple first-order reaction, as also does the fact that the " constant " decreases when $[NO_2]/[C_2H_4]$ is large. The process has an activation energy of 17 kcal., which is not very different from that found for the oxidation of aldehydes by nitrogen dioxide.

The mechanism put forward above is very similar to that suggested by Pollard and Wyatt (*loc. cit.*) for the oxidation of formaldehyde. Although the latter is kinetically of the second order, this could be so if, in Scheme I, $k_2 < k'_3[NO_2]$ for the analogous reactions with formaldehyde. The " dinitro " derivative of formaldehyde would probably not exist as such. On the other hand, McDowell and Thomas (*loc. cit.*) favour hydrogen abstraction as the initial reaction of nitrogen dioxide with aldehydes. Hydrogen abstraction is unlikely as a mechanism for the ethylene reaction, both because of the experimental evidence on the pressure and because the C–H bond in ethylene is much stronger than C–H bond in formaldehyde. Addition has also been shown to be the probable first step.

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