475. *Kinetics, Mechanism, and Chemistry of the Thermal Decomposition of Ammonium Dichromate.*

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Kinetics of the decomposition *in vacuo* of well-formed single crystals of ammonium dichromate at 180—215° showed three consecutive processes: (1) an induction period corresponding to nucleation, (2) an autocatalysis consistent with a Prout–Tompkins chain mechanism, and (3) a constant-area interface process. In (2) the symmetry of the sigmoid pressure–time and weight decrease–time curves leads to a single value of the rate constant in the Prout–Tompkins equation in contrast to the two values required for other substances. During decomposition, the crystals became deep red, then gradually darkened owing to large numbers of submicroscopic nuclei to a highly cracked black solid amorphous to *X*-rays. In addition, a few black diamond-shaped nuclei developed on the crystal surfaces but only in the early stages, and were responsible for a very small fraction of the total decomposition. The induction period for crystals kept in a desiccator over phosphoric oxide decreased with increasing storage time, becoming zero after two years, and the acceleration stage of the autocatalysis then corresponded to spherical growth of a constant number of nuclei. These effects of ageing are compared with those in mercury fulminate. The equation for the reaction at 195·5° was determined; the composition of the black solid corresponded formally to $Cr_2O_3,0{\cdot}88H_2O,0{\cdot}047N_2O,0{\cdot}15O_2$. Nitrogen, nitrous oxide, and water were evolved throughout the reaction, but evolution of ammonia ceased after the autocatalytic stage. When prepared at 215°, the black solid contained no nitrous oxide but the same amount of extra oxygen, and its decomposition at 220—385° suggested that the extra oxygen was present as Cr_2O_5. Infrared spectra showed the formation of an intermediate which may contain nitrite and nitrate groups and reaches a maximum concentration at the end of the autocatalysis. Further evidence in support of an intermediate has been obtained from electrical-conductivity changes during decomposition of highly compressed pellets of the dichromate. A possible structure is suggested for it.

Thermal decomposition at 195—218° of very small, rapidly grown crystals of ammonium dichromate occurs [1] in two main stages: (1) an autocatalytic stage best represented by the modified Prout–Tompkins equation [2] $\log_{10} p/(p_t - p) = k \log_{10} t + \text{const.}$, where p_t is the pressure, at the end of the stage, of gaseous products not absorbed by phosphoric oxide, followed by (2) a process of constant rate at an interface. We further investigated the decomposition in view of (*a*) the difference between these results and those of Fischbeck and Spingler [3] who reported a contracting-sphere mechanism [4] for most of the decomposition, (*b*) the failure to secure 100% decomposition according to their reaction scheme [5] $(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3,H_2O + 3H_2O + N_2$, and (*c*) the conflicting reports [6] as to the nature of the gaseous and solid products. Kinetic measurements on well-formed single crystals were supplemented by microscopical observations, analysis of products, and measurements of electrical conductivity and infrared absorption.

Experimental and Results

Growth of Crystals.—Single crystals free from striae and growth steps were obtained as rhombs or hexagonal tablets of weight 5—20 mg. by slow evaporation in air at room temperature of solutions initially saturated with the " AnalaR " salt at 30°. The first crop, consisting

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[1] Taylor, *J.*, 1955, 1033.

[2] Prout and Tompkins, *Trans. Faraday Soc.*, 1946, **42**, 468.

[3] Fischbeck and Spingler, *Z. anorg. Chem.*, 1939, **241**, 209.

[4] Garner, " Chemistry of the Solid State," Butterworths, London, 1955, p. 202.

[5] Fischbeck and Spingler, *Z. anorg. Chem.*, 1938, **235**, 183.

[6] (*a*) Moles and Gonzalez, *Anales Fis. Quim.*, 1923, **21**, 204; (*b*) Ball, *J.*, 1909, 87; (*c*) Ref. 5; (*d*) Harbard and King, *J.*, 1938, 955.

invariably of large, very imperfect crystals, was filtered off; the subsequent crop contained many small crystals from which suitable specimens were selected by hand with the aid of a lens. The crystals were dried by gentle pressure between filter papers, and either used immediately or stored in a desiccator over phosphoric oxide. Only very rarely were good crystals heavier than 20 mg. obtained. Fresh crystals, after being crushed and dried at 100°, lost 0·5% in weight. For comparative kinetic experiments, a few crystals, visibly very imperfect, of about 10 mg. were rapidly grown by the procedure in ref. 1.

Preparation of Pellets.—For electrical-conductivity measurements, and some thermal decompositions, ground recrystallised $(NH_4)_2Cr_2O_7$ was compressed at about 3 tons/sq. inch into strong hard cylindrical pellets, 6·52 mm. in diam. and 2—3 mm. in height, in which spurious electrical effects due to poor contacts between individual particles [7] were probably minimised.

Microscopical Observations.—Crystals, when heated from 170° to 230° on a hot-stage microscope either in air or in a small evacuated tube provided with a flat window, showed two phenomena: (1) surface growth of small black diamond-shaped nuclei whose long diagonals were always parallel to the *b* axis of the crystals; these diagonals were characterised by a pronounced crack with several others approximately at right-angles; (2) irreversible deep-red coloration throughout the crystal, followed by gradual darkening due to submicroscopic diffuse nuclei [8] to give finally a black lustrous solid of essentially the same shape as the original crystal; the final solid was riddled with cracks mostly aligned parallel to the original *b* axis. Occasionally, depending on the rate of heating and size of the crystals, the latter shattered into two or three pieces during decomposition. *X*-Ray measurements with single crystals showed that the colour change to deep red was not due to a polymorphic transformation. The diamond-shaped nuclei never developed to cover more than half of the surface before the darkening had rendered the crystal completely black and opaque. Experiments at 195·5° in the thermal decomposition apparatus showed that the opaque stage was reached at about 15% decomposition and, since the diamond-shaped nuclei appeared only on the surface, the main decomposition was apparently associated rather with the darkening process than with the discrete nuclei.

Nature of the Gaseous Products.—Sufficient ammonium dichromate was decomposed slowly at 196° in a small evacuated tube attached to a liquid-nitrogen trap to give a non-condensable gas of pressure 10 mm. Hg, the volume being 70 c.c. By gas chromatography on a silica gel column with nitrogen as the carrier gas and a thermal conductivity gauge as detector, the non-condensable gas was also found to be nitrogen. On flushing the condensate in the trap into the column, appreciable quantities of nitrous oxide were found; its identity was further confirmed by its infrared absorption. Water and ammonia were detected in the trap in a separate experiment by standard tests. No other gaseous product was found unless the dichromate was allowed to decompose explosively at higher temperatures, in which case with a charcoal column a little nitric oxide was detected also. Furthermore, in the liquid-nitrogen trap at the end of some of the weight-loss experiments with 100 mg. of dichromate, coupling tests [9] detected less than 5 μg. of nitrite and nitrate ions.

Procedure for Thermal Decomposition.—(1) The apparatus used to determine the kinetics of evolution of the gaseous products at 188—215° was similar to that described.[1] All samples, normally single crystals (5—20 mg.), were evacuated overnight at less than 10^{-6} mm. Hg before decomposition. At a given temperature, very similar pressure–time curves were obtained whether the platinum bucket containing the sample was loosely closed or left open. In experiments with a phosphoric oxide trap immediately following the reaction vessel to absorb water and ammonia, the combined pressure of nitrogen and nitrous oxide was measured (not nitrogen alone as previously believed [1]), while in others use of a liquid-nitrogen trap condensed all gases except nitrogen. The volume of the system could be varied between 600 and 6684 c.c. so that the final pressure was normally about 0·1 mm. Hg after 24 hr. Replacement of the McLeod by a Bourdon gauge and omission of cold and absorption traps allowed the pressure of the total gaseous products to be measured in a system of volume 600 c.c. which gave a final pressure of about 3 mm. Corrections to the measured pressures to allow for temperature differences in the system were calculated to be of similar size to the experimental errors, and were therefore omitted.

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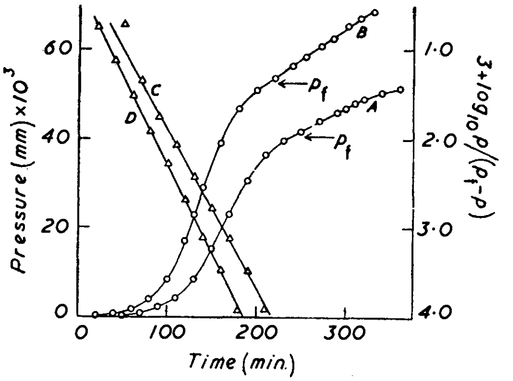
[7] Wagner and Hantlemann, *J. Chem. Phys.*, 1950, **18**, 72.
[8] Ref. 4, p. 187.
[9] Rider and Mellon, *Analyt. Chem.*, 1946, **18**, 96; Woodward, *Analyst*, 1953, **78**, 727.

The rate of evolution of ammonia at 195·5° was determined by decomposing about 0·5 g. of crystals in five successive stages with a liquid-nitrogen trap after the reaction vessel. The autocatalytic part of the decomposition was divided, by use of measurements of nitrogen pressure, into four roughly equal stages, while the fifth stage included the remainder of the decomposition up to a maximum time of 24 hr. After each stage the reaction was halted by raising the sample to the cold part of the reaction vessel, and the ammonia in the trap was then determined by addition, while the trap was still cold, of excess of hydrochloric acid and back-titration with sodium hydroxide solution.

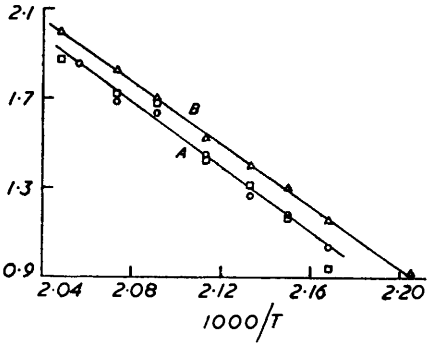
(2) To follow the loss in weight of the solid during decomposition, a McBain–Bakr balance was used, the spring being of 0·25 mm. diam. beryllium–copper wire. The sample, in a platinum-foil bucket, was suspended in the hot zone of the reaction vessel near a thermocouple by means of a 30 cm. fine glass rod attached to the spring, whose extension was observed with a microscope provided with an eyepiece scale. The sensitivity of the balance required a sample weight of about 100 mg. (several crystals or a small pellet) and the useful temperature range was 188—200°. Above 200° the rapid rate and occasional splitting of the crystals caused violent oscillation of the spring so that rate measurements were impossible. After raising the electric furnace round the reaction vessel the heating period was not less than 30 min., but fortunately only a small fraction of the total (*ca.* 32%) decrease in weight occurred during this time. Experiments were conducted: (*a*) with continuous evacuation and a liquid-nitrogen trap between balance and pump, or (*b*) with the pressure of one or more of the gaseous products building up in the balance after preliminary evacuation to 10^{-3} mm. Hg. In (*b*), a liquid-nitrogen trap allowed only nitrogen to accumulate, while phosphoric oxide or barium oxide in a small dish placed just above the spring allowed nitrogen and nitrous oxide, or these and ammonia, respectively, to accumulate. Tests showed that barium oxide under the experimental conditions absorbed only minute traces of ammonia. The volume of the balance and trap being about 650 c.c., the final pressures reached in (*b*) were 10—20 mm. Hg.

FIG. 1.



Curves *A* and *B*: Pressure–time curves for evolution of N_2 and $N_2 + N_2O$ respectively at 195·5°. Lines *C* and *D*: Prout–Tompkins equation plots for curves *A* and *B* respectively.

FIG. 2.



Line *A*: Activation-energy plot for autocatalytic stage: ○ N_2 runs, □ $N_2 + N_2O$ runs. Vertical axis $3 + \log_{10} k$. Line *B*: Activation-energy plot for nucleation stage. Vertical axis $3 + \log_{10} 1/\tau$.

Kinetics of Evolution of Nitrogen and of Nitrogen plus Nitrous Oxide.—Pressure–time curves for individual freshly prepared crystals were determined at seven temperatures between 188° and 215°. Despite great care in the selection of crystals, rates were reproducible generally only to within about 20%, so several runs were carried out at each temperature and the results averaged to determine activation energies. All pressures were corrected to a standard initial sample weight of 10 mg. and a reaction volume of 6684 c.c. by assuming direct proportionality between pressure and initial weight. This was justified by the observation at 195·5° that both the maximum rate in the autocatalytic stage and the later constant rate were directly proportional to the initial crystal weight over the range 2—20 mg. At a given temperature, the corrected pressures at any given stage in the decomposition were reproducible to better than 5%. For all experiments the pressure–time curves were very similar to those already published [1] except that induction periods were much longer (10—70 min., decreasing with rise in temperature) and the sigmoid part of the curves could best be represented by the original Prout–Tompkins equation [10] $\log_{10} p/(p_f - p) = kt +$ const. where p_f is the pressure at the end of the sigmoid. Fig. 1 is typical for these experiments and shows that a single value of k is required for the whole of the sigmoid in both the N_2 and $N_2 + N_2O$ runs, in contrast to the two values found in other decompositions.[11] A single value for k requires the sigmoid curve to be symmetrical with the maximum rate at the mid-point; experimentally, these conditions were closely fulfilled. Mean values of $\log_{10} k$ are plotted in Fig. 2, line A, which leads to an activation energy for both the N_2 and $N_2 + N_2O$ experiments of 33 ± 1·5 kcal./mole. Similar plots of the constant rates gave an activation energy of 41 ± 2 kcal./mole both for evolution of N_2 and for that of $N_2 + N_2O$. In the nitrogen runs, irrespective of temperature, the final pressure after 24 hr. corresponded to 54 ± 2% of the theoretical nitrogen in the dichromate and p_f to 38 ± 2%. For $N_2 + N_2O$, the final pressure at 188° was equivalent to 73 ± 2% of the theoretical nitrogen content, and rose to 83 ± 2% at 205°, remaining constant thereafter up to 215°. Thus 19—29% ±4% of the nitrogen in the dichromate was evolved as nitrous oxide, and the increase with rising temperature was due mainly to extra gas evolved during the indeterminate decay stage which followed the constant-rate process. The average of several experiments at 195·5° showed that 0·54 mole of nitrogen and 0·24 mole of nitrous oxide were obtained from each mole of dichromate. Attempts to construct reliable nitrous oxide pressure–time curves by taking the difference between the pressures of corresponding $N_2 + N_2O$ and N_2 curves failed: it was impossible to relate accurately the time scales of separate experiments owing to the difficulty of determining induction periods to better than ±5 min. Interruption of the decomposition (cf. ammonia determinations) during either the autocatalytic or constant-rate stages did not influence the shape of the nitrogen pressure–time curve provided allowance was made for the short heating periods, thus showing that energy chains were absent.[12]

FIG. 3. *Evolution of nitrogen and ammonia at* 195·5°.

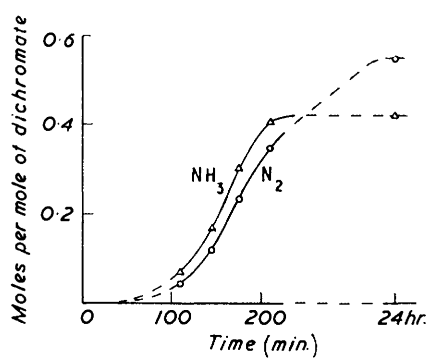
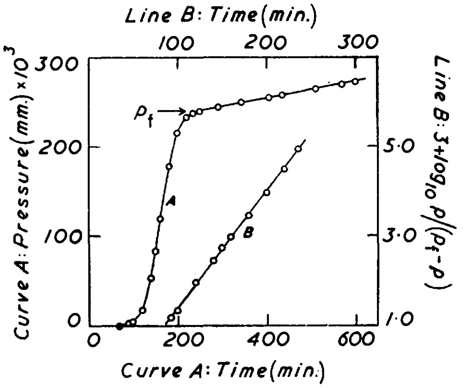


FIG. 4.



Curve A: Pressure–time curve for evolution of total gases at 195·5°. Line B: Prout–Tompkins equation plot for curve A.

Rapidly grown crystals gave much faster and less reproducible rates and, as earlier found,[1] the modified Prout–Tompkins equation [2] (*i.e.*, with $\log_{10} t$ in place of t) gave the best fit for the autocatalytic stage.

Evolution of Ammonia and Water.—Typical results for a stepwise decomposition at 195·5° (Fig. 3) show that virtually all the ammonia is evolved during the autocatalysis. The average of four experiments gave the total ammonia as 0·41 mole per mole of dichromate. The total loss in weight of the dichromate, less the weight of ammonia and of nitrogen and nitrous oxide determined above, corresponded to 2·6 moles of water per mole of dichromate. Attempts to determine the water by weighing the contents of the trap and allowing for the condensed

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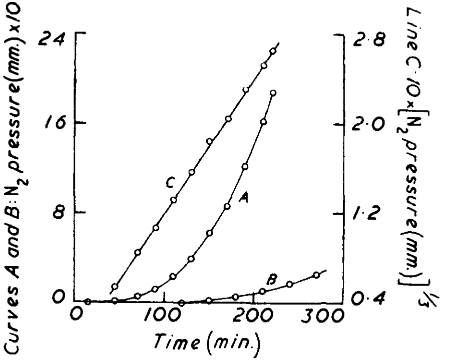
[10] Prout and Tompkins, *Trans. Faraday Soc.*, 1944, **40**, 488.
[11] Tompkins and Young, *Ann. Reports*, 1953, **50**, 73, 77, 79.
[12] Ref. 4, p. 195; Tompkins and Young, *Trans. Faraday Soc.*, 1956, **52**, 1245.

ammonia and nitrous oxide gave undoubtedly high results, owing probably to distillation into the trap of small unknown weights of mercury from the McLeod gauge.

Kinetics of Evolution of Total Gaseous Products.—Typical results at 195·5° are given in Fig. 4, in which pressures have been corrected as in the nitrogen-evolution runs. Notable features are the very good fit of the Prout–Tompkins equation for the autocatalytic stage, and the extension of the constant-rate stage to about 6 hr. compared with about 2 hr. for N_2 and $N_2 + N_2O$ experiments. Comparison with curves for the other gases showed that water, in contrast to ammonia, was evolved throughout the decomposition, but totalled only 2·0 moles per mole of dichromate instead of 2·6 moles as calculated above. In view of the low partial pressures involved, the loss is believed to be due to adsorption on the glass surfaces, and the value 2·6 is preferred.

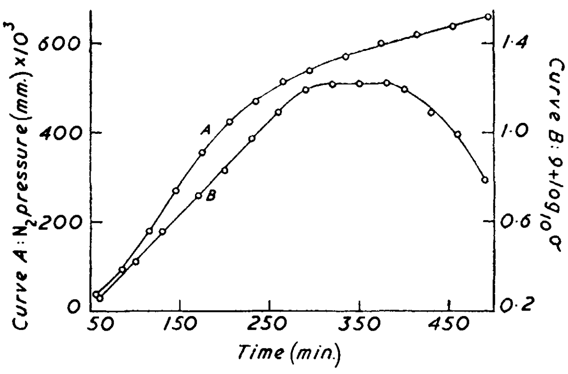
The Induction Period.—Induction periods were arbitrarily defined as the time τ (min.) required for the nitrogen pressure to reach 10^{-4} mm. Hg, the rate during the period being taken as $1/\tau$. For well-formed freshly grown crystals, values of τ showed considerable scatter, but mean values at a given temperature did not appear to be influenced significantly by crystal habit or weight, and the temperature coefficient of $1/\tau$ gave an activation energy of 32 ± 1 kcal./mole (Fig. 2, line *B*). At the end of the induction period, crystals were very deep red, and after 1% decomposition had perceptibly darkened but no diamond-shaped nuclei had appeared. *X*-Ray rotation photographs of a crystal before and after 1% decomposition were identical. Rapidly grown crystals gave much shorter, and sometimes zero, values of τ. Saturated ammonium dichromate solutions, after exposure to daylight for several weeks at room temperature, were noticeably darker in colour and yielded by slow growth dark red crystals which decomposed without an induction period. The fact that occasionally τ was zero showed that induction periods were not significantly affected by delays in the diffusion of gaseous products from the reaction vessel to the rest of the system. Qualitative measurements of the visible absorption spectrum of crystals with a Unicam S.P. 600 spectrophotometer showed that no new absorption bands in the range 5500—10,000 Å appeared either during the induction period or after short decomposition at 195·5°. Well-formed, sufficiently thin crystals could not be obtained to permit measurements below 5500 Å where the absorption is very strong.[13]

FIG. 5. *Change in kinetics at* 180·5° *after storage over phosphoric oxide.*



Curves *A* and *C*: Crystal stored for 2 years.
Curve *B*: Freshly prepared crystal.

FIG. 6. *Nitrogen pressure–time and specific conductivity–time curves at* 186·3°.



Effect of Ageing over Phosphoric Oxide.—Well-formed crystals, when stored over phosphoric oxide, progressively lost their original brilliance, edges and corners became slightly rounded, and the induction period at 180·5° decreased from 120 min. to zero after 2 years' storage. At 180·5° the acceleration part of the autocatalysis for a 2 years-old crystal was faster than that for a new one (see Fig. 5, where pressures have been corrected as in the nitrogen-evolution runs), and best fitted the relation $p(N_2) \propto t^3$ as far as the maximum-rate stage (35% decomposition). Crystals up to 1 year old yielded the relation $p(N_2) \propto t^n$ up to 20—25% decomposition over a range of temperatures, n varying between 2·5 and 5·5. The decay part of the sigmoid curve

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[13] Englis and Wollerman, *Analyt. Chem.*, 1952, **24**, 1983.

always fitted the Prout–Tompkins equation with the same value of k as for un-aged crystals at the same temperature. The constant rates for aged crystals were less reproducible than for new crystals, but age had no significant effect on the percentage decomposition at the end of either the sigmoid or the constant-rate stages.

Effect of Ultraviolet and γ-Irradiation.—Exposure of crystals in air to ultraviolet light for several hours had no detectable effect. Crystals after exposure *in vacuo* for 4 months to ^{60}Co γ-rays of low intensity had become very dark red, and gases were evolved up to a point corresponding to not more than the end of an induction period. However, on subsequent thermal decomposition at 195·5°, an induction period only slightly less than normal occurred and, while the autocatalytic stage fitted the Prout–Tompkins equation, two values of k were required: 0·023 up to the maximum-rate stage and 0·015 thereafter, compared with 0·0175 for the single k of un-irradiated crystals at the same temperature.

Loss-in-weight Studies.—Experiments at four temperatures between 188° and 200° with continuous evacuation gave weight decrease–time curves having the same features as the pressure–time curves in Fig. 1, but rates were generally less reproducible. The autocatalysis could again best be represented by the Prout–Tompkins equation with a single value of k and had an activation energy of 35 ± 3 kcal./mole. For the constant-rate stage the activation energy was 41 ± 3 kcal./mole. Decomposition of pellets gave similar curves and no evidence for a contracting-cylinder type of process.[14] Slight but distinct catalysis of the decomposition in the early stages by the black solid product was observed with a pellet prepared from an intimate mixture of the dichromate with 10% by weight of the black solid. At 192°, decompositions where one or more of the gaseous products accumulated showed that the reaction was not inhibited by nitrogen or nitrous oxide, but was inhibited appreciably by ammonia and very strongly by water. Since inhibition was absent from the total-pressure experiments and the final pressures were about 3 mm. Hg, pressures greater than the latter appear necessary to give a significant effect.

Composition of the Solid Products.—The final black solid obtained at 195·5°, although pseudomorphous with the original crystals, was amorphous to X-rays. The chromium was determined volumetrically after fusion with sodium peroxide,[15] and the water by roasting the solid at 800° *in vacuo* in a silica tube attached to a phosphoric oxide tube, whose increase in weight was noted (Found: Cr, 60·1%; H_2O, 8·1%). Two other gases evolved during the roasting were shown by gas chromatography to be nitrous oxide and oxygen. Their quantities were determined by heating the solid in the thermal decomposition apparatus and noting the pressures developed; a phosphoric oxide trap was used to absorb water and where necessary a liquid-oxygen trap to condense nitrous oxide. All the latter was evolved by 230°, but no oxygen until 385°, at which it was evolved explosively and then partially adsorbed on the solid (Found: N_2O, 1·2%; O_2, 2·8%). The black solid obtained at 215° was found on similar treatment to evolve no nitrous oxide but the same amount of oxygen. After treatment at 385° the solid contained 67·4% of chromium (Calc. for Cr_2O_3: 68·4%) and, as shown by X-ray powder photographs, had partially crystallised as Cr_2O_3.

After 20—30% decomposition at 195·5°, the dichromate was black to the eye but still partially soluble in water to give a greenish-yellow solution. Spectrophotometry [13] showed the solution to contain 1·5% of the total chromium as chromic ions. At the end of the autocatalytic stage (70% decomposition) the solid was completely insoluble in water. At no stage in the decomposition could any nitrite or nitrate ions be extracted from the solid with water, hydrochloric acid, or sodium hydroxide solution.

Electrical-conductivity Measurements.—The electrical equipment and conductivity cell were similar to those of Jacobs,[16] except that the direction of the applied potential (1—120 v D.C.) was reversed manually. Full details of the electrical circuit were given by Simpson.[17] The empty evacuated cell at 200° had a resistance greater than 10^{16} ohms, while the range of resistances measured for dichromate pellets was 10^7—10^{13} ohms. From 37° to 162° the specific conductivity of pellets *in vacuo*, after 24 hours' preliminary evacuation at room temperature, was given by $\sigma = 9{\cdot}4 \exp(-20{,}400/\boldsymbol{RT})$ ohm^{-1} cm.$^{-1}$ irrespective of the direction of the applied

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[14] Cf. ref. 4, p. 200.

[15] Cumming and Kay, " Quantitative Chemical Analysis," Oliver and Boyd, Edinburgh, 10th edn., p. 140.

[16] Jacobs, *J. Sci. Instr.*, 1953, **30**, 204.

[17] Simpson, Ph.D. Thesis, University of Edinburgh, 1957.

voltage, results being reproducible within ±2%. Both the activation energy and the pre-exponential factor are reasonably characteristic of structure-sensitive conduction.[18] The fact that the same resistance values were obtained at corresponding temperatures on heating and cooling showed that the pellet had not significantly decomposed. Over the same range of temperature the activation energy for conduction was 12·4 ± 1 kcal./mole after the pellet had been allowed to decompose for 24 hr. at 180°.

By connecting the vessel containing the conductivity cell to the thermal-decomposition apparatus, conductivity–time and nitrogen pressure–time curves for dichromate pellets were determined simultaneously. The apparatus was evacuated for 24 hr. at room temperature before the furnace was raised round the reaction vessel, and since the cell was freely suspended in the vessel by a thin wire the heating period was about 40 min., compared with the total decomposition time of 12 hr. at 186·3°. At higher temperatures appreciable decomposition occurred during the heating, while below 180° the reaction was prohibitively slow. Results at 186·3° are shown in Fig. 6, the exponential rise in σ with time being typical for the ten pellets examined. At the same temperature, experiment with a thermocouple (48 gauge wire) embedded in a pellet showed that no self-heating occurred during decomposition.

Infrared-absorption Measurements.—A Hilger H 800 spectrophotometer with a rock-salt prism was used, calibration for frequency being carried out daily with polystyrene. An accuracy of ±2 cm.$^{-1}$ is claimed. Spectra were determined for ammonium dichromate before and after its complete decomposition (24 hr.) at 195·5°, and also at the end of each of seven roughly equally spaced stages in the reaction. New absorption peaks at 1270 and 825 cm.$^{-1}$ gradually developed, reached maximum intensity at the end of the autocatalytic stage, and then decayed to zero by the end of the decomposition. By the end of the autocatalytic stage the known strong peak of ammonium ions [19] at 3170 cm.$^{-1}$ had virtually disappeared, but a peak at 1385—1400 cm.$^{-1}$, initially strong and which is common to the ions NH_4^+, NO_3^-, and NO_2^-, retained a medium intensity. The latter peak was still evident, though very weak, even at the end of the decomposition. Spectra obtained from potassium bromide discs and Nujol mulls gave the same results. No evidence was obtained to suggest that any of the above peaks were due to adsorbed ammonia or nitrous oxide. For comparison, spectra of sodium nitrite and nitrate and ammonium nitrate were determined in potassium bromide discs and showed the following absorptions (cm.$^{-1}$, for s, m, w, see Table): NO_2^-: 2550 w, 1380 m, 1270 s; NO_3^-: 1385 s, 825 m; NH_4^+: 3170 s, 1400 s (cf. refs. 19, 20). Thus in the dichromate spectra the 1270 cm.$^{-1}$ peak suggests the formation of nitrite ion as one of the species in an intermediate product, while the 825 cm.$^{-1}$ peak (together with the persistence of the peak at 1385—1400 cm.$^{-1}$ after the disappearance of the peak at 3170 cm.$^{-1}$) suggests nitrate. It also seems likely that most of the ammonium ions have decomposed by the end of the autocatalysis. However, the failure to extract nitrite or nitrate ions from the solid products of decomposition shows that, if these ions are present, they do not occur in a soluble form and may therefore be strongly co-ordinated in the intermediate. Co-ordination should alter the absorption frequencies compared with those of the free ions,[21a] and in an attempt to elucidate the nature of the co-ordination, spectra of $[Cr(NH_3)_5H_2O](NO_3)_3,NH_4NO_3$ (*A*), $[Cr(NH_3)_5NO_2](NO_3)_2$ (*B*), $[Cr(NH_3)_5NO_3](NO_3)_2$ (*C*), and $[Cr(NH_3)_6](NO_3)_3$ (*D*) were determined in Nujol mulls. Peaks within the range obscured by Nujol absorptions were determined with potassium bromide discs and are marked with an asterisk. When the rock-salt plates were protected from the mulls with polystyrene films [21b] the spectra were unchanged. Results are given in the Table.

Frequency (*cm.*$^{-1}$, *s* = *strong*, *m* = *medium*, *w* = *weak*, *v* = *very*).

A	*B*	*C*	*D*	*A*	*B*	*C*	*D*
1763 w	1766 w	1765 w	1762 w	—	1228 s	—	—
1630 m	1628 m	1627 m	1633 m	1049 w	—	1054 vw	1038 m
—	1487* s	1501 s	—	—	1017 s	1022 s	—
1395* vs	1390* vs	1379* vs	1386* s	—	—	—	954 m
1312* s	1302* s	1309* s	1304* s	824 m	833 s	836 m	831 m
—	—	1277 s	—	753 s	772 s	781 s	779 s

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[18] Jacobs and Tompkins, *Quart. Reviews*, 1952, **6**, 238.

[19] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

[20] Weston and Brodasky, *J. Chem. Phys.*, 1957, **27**, 683.

[21] (*a*) Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222; (*b*) Gatehouse, *Chem. and Ind.*, 1957, 1351.

Frequencies near 1620, 1310, and 770 cm.$^{-1}$ have been reported [22] for ammonia co-ordinated to Cr^{3+} ions, and those at 1530—1480, 1290—1250, and 1034—970 cm.$^{-1}$ are characteristic of nitrato-complexes.[21] If any nitrite or nitrate groups are present in the intermediate product, they appear not to be co-ordinated to Cr^{3+} normally. For *A*, *B*, *C*, and *D* several of the peaks in Nujol mull spectra were displaced by up to 18 cm.$^{-1}$ in spectra from potassium bromide discs.

DISCUSSION

Reaction Kinetics.—The results for un-aged crystals in both the pressure–time and weight decrease–time experiments, together with the appearance of many cracks in the crystals during decomposition, confirmed the earlier view [1] that the autocatalytic stage is consistent with a branching and interfering chain mechanism of the Prout–Tompkins type with an activation energy of 33 ± 1·5 kcal./mole. The chain process is followed by a reaction at an interface of constant area of significantly higher activation energy (41 ± 2 kcal./mole for single well-formed crystals and 38 ± 2 kcal./mole for small imperfect crystals [1]). In the autocatalysis the results fit the original Prout–Tompkins equation [10] better than the modified equation [2] required in the earlier work. (In the former equation, the chain-branching coefficient is assumed to be independent of time, and in the latter inversely proportional to it.) This feature may well be due to the use here of well-formed crystals where the slower rates and longer induction periods indicate fewer reaction chains, and where a more nearly constant branching coefficient would thus be expected. The pronounced extension of the constant-rate stage in the total-pressure experiments suggests that at low pressures water and ammonia act to preserve the reaction interface of constant area, although the weight-decrease experiments clearly showed that at higher pressures water, and to a smaller extent ammonia, inhibit the decomposition. Since, except for the ammonia determinations, the different types of kinetic experiment gave very similar results, it appears that nitrogen, nitrous oxide, and water are all formed in one set of chemical processes during the autocatalysis and in a different set during the constant-rate stage. The reactions giving free ammonia are probably quite different although the corresponding activation energy is unknown.

The two main stages of the reaction discussed above are preceded by a nucleation stage, and in spite of the considerable scatter in induction periods, the activation energy of the stage is believed to be 32 ± 1 kcal./mole. The latter, being not greater than the values for the other two stages (the pre-exponential factors are unknown), is consistent with the observation that by far the greater part of the decomposition is associated with a general darkening of the solid by large numbers of diffuse nuclei rather than with the growth of relatively few discrete nuclei.[8] The amount of decomposition caused by γ-irradiation of crystals was very small owing partly to the relatively low dose rate, and although the induction period in the subsequent thermal decomposition was only slightly reduced compared with that in un-irradiated crystals, the probability of chain branching in the acceleration stage (given by k in the Prout–Tompkins equation) had increased significantly.

The kinetics found for fully aged single crystals up to the maximum-rate stage suggest spherical growth of a constant number of nuclei. This change in kinetics compared with those for fresh crystals is parallel to that found when mercury fulminate is aged [23] and may have a similar explanation: ageing is considered to change the grain structure of the crystals as a result of slight decomposition such that a large number of non-contiguous blocks are formed, thus preventing the propagation from block to block of the reaction chains which give rise to Prout–Tompkins kinetics. The cubic relation then describes the kinetics of the reaction occurring in the individual blocks. However, with ammonium dichromate, in contrast to the fulminate, no decomposition could be detected during

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[22] Kobayashi and Fujita, *J. Chem. Phys.*, 1955, **23**, 1354; Svatos, Sweeny, Mitzushima, Curran, and Quagliano, *J. Amer. Chem. Soc.*, 1957, **79**, 3313.

[23] Bartlett, Tompkins, and Young, *J.*, 1956, 3323; Tompkins and Young, *Discuss. Faraday Soc.*, 1957, **23**, 202.

ageing, but only a change in the physical appearance of the crystals. We suggest therefore that the structural change may have been due to the loss of traces of water (and maybe of ammonia) during storage over phosphoric oxide. This would imply either that chain branching across blocks in un-aged crystals occurs *via* water and/or ammonia molecules, or that loss of traces of these molecules from grain boundaries results in the collapse of bridges composed essentially of dichromate molecules. Since, after the maximum rate stage, the decay part of a normal Prout–Tompkins chain process occurred, it may be either that ageing did not affect the whole crystal, or that, on heating, a type of annealing process involving the reaction products water and ammonia took place, so that continuity between the blocks was restored.

Chemistry of the Decomposition.—The equation for the decomposition at 195·5° can be written as

$$(NH_4)_2Cr_2O_7 \longrightarrow \text{Black solid} + 0{\cdot}54N_2 + 0{\cdot}24N_2O + 0{\cdot}41NH_3 + 2{\cdot}6H_2O,$$

the loss in weight of the dichromate being close to 32%. The black solid formed at the same temperature can be shown to correspond formally to $[Cr_2O_3,0{\cdot}88H_2O,0{\cdot}047N_2O,0{\cdot}15O_2]$; it loses 12% in weight when roasted to give essentially chromic oxide. Calculation showed that the nitrogen balance for the reaction is correct to within 3%; in view of the experimental errors this is satisfactory and shows that no significant nitrogen-containing product has been missed.

The above equation shows that approximately one in every five ammonium ions decomposes to give free ammonia, probably by the reactions (cf. ammonium perchlorate [24]):

$$NH_4^+ + Cr_2O_7^{2-} \longrightarrow NH_4 + Cr_2O_7^- \longrightarrow NH_3 + HCr_2O_7^-$$

Since virtually all of the ammonia is evolved during the autocatalytic stage, and in view of the infrared absorption data, the other 80% of the ammonium ions have probably been oxidised in other ways before the end of the stage, though the solid must still possess a source of hydrogen (perhaps as NH_2 groups) because water continued to be evolved up to the end of the decomposition.

Infrared absorptions indicate the formation of an intermediate which may contain nitrite and nitrate groups and whose concentration reaches a maximum by the end of the autocatalysis, the solid then being completely insoluble. Since it seems most unlikely that ammonium nitrite or nitrate could be present in the decomposing solid, it is suggested that the intermediate consists of chains of alternating chromium and oxygen atoms to which nitrite and nitrate (and maybe NH_2) groups are linked (cf. ref. 25). The formation of such a chain structure seems reasonable in view of the occurrence in the original salt of chains of dichromate ions with ammonium ions conveniently placed near the ends of the former ions.[26] Although nitrogen, nitrous oxide, and water are evolved at all stages of the decomposition, the formation of the intermediate evidently predominates during the autocatalytic stage, and its decomposition during the subsequent stages. The evidence for the slight occurrence of $Cr_2O_7^{2-} \longrightarrow Cr^{3+}$ in the early stages of the decomposition suggests that Cr^{3+}, which can be extracted with water, may also be a transient intermediate, but one whose concentration is always low. On the other hand, the Cr^{3+} may have arisen indirectly *via* the soluble Cr_3O_8 [27] produced by decomposition of the acid which is formed when ammonia is evolved. The infrared spectrum of the final black solid obtained at 195·5° indicates the presence of a small concentration of nitrate groups but the absence of nitrite; and since the solid when further heated yields a little nitrous oxide, the latter may arise preferentially from reactions of the nitrate groups and nitrogen from the

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[24] Bircumshaw and Newman, *Proc. Roy. Soc.*, 1955, *A*, **227**, 228.

[25] Schmitz-Du Mont, *Z. Elektrochem.*, 1956, **60**, 866; Bailar, "Chemistry of the Coordination Compounds," Reinhold, New York, 1956, p. 448.

[26] Byström and Wilhelmi, *Acta Chem. Scand.*, 1951, **5**, 1003.

[27] Schwartz, Fankuchen, and Ward, *J. Amer. Chem. Soc.*, 1952, **74**, 1676.

nitrite (and/or NH_2) groups. The electrical conductivity of pellets during decomposition suggests the exponential production with time of current carriers which are later destroyed, and may therefore be related to the intermediates discussed above.

The explosive evolution of oxygen at about 385° from the black end-product is characteristic of the decomposition of the oxide Cr_2O_5,[6d, 28] which may thus be one of the decomposition products of the intermediates or of the acid formed when ammonia is evolved. The quantity of oxygen evolved shows that the black solid may contain about 16% by weight of Cr_2O_5. After roasting of the black solid, the green product, in view of its high oxygen content compared with Cr_2O_3, may contain about 10% by weight of CrO_2, because the limits of deficiency or excess of oxygen in Cr_2O_3 are very narrow.[29]

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[28] Glemser, Hauschild, and Trupel, *Z. Anorg. Chem.*, 1954, **277**, 113.

[29] Bevan, Shelton, and Anderson, *J.*, 1948, 1729.