

Heterogeneous Oxidation of Hydrazine by Barium Chromate

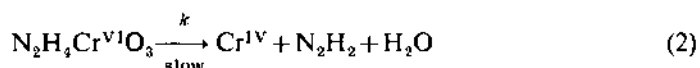
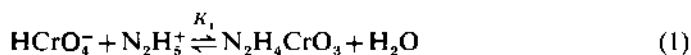
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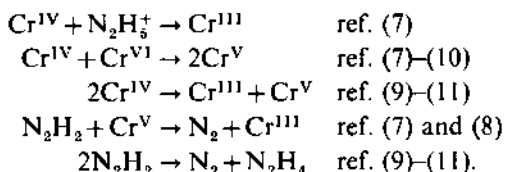
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The kinetics of the heterogeneous oxidation of hydrazine by barium chromate in aqueous suspensions has been studied. The results obtained on changing the concentration of hydrazine and the mass of barium chromate show that the reaction proceeds through a fast chemisorption equilibrium in which a complex is formed between chromium atoms on the surface of the particles and hydrazine. A Langmuir-type analysis of the data gave an adsorption equilibrium constant of $1.14 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$ and a rate constant k for the decomposition of the adsorption complex of $1.1 \times 10^{-2} \text{ s}^{-1}$. A comparison between this heterogeneous reaction and the corresponding homogeneous reaction shows that the presence of the interface leads to acceleration by a factor of *ca.* 10^6 . It is shown that this acceleration is due in part to the increased concentration of the complex at the interface ($[\text{adsorption complex}]/[\text{complex}]_{\text{hom}} = 10^4$) and to an increase in its reactivity ($k_{\text{het}}/k_{\text{hom}} = 10^2$). A possible explanation for this enhanced reactivity is given.

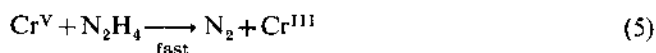
The mechanism of the oxidation of hydrazine in homogeneous solutions has been the subject of numerous studies and has been reviewed by Audrieth and Ogg¹ and by Bottomley.² In the case of simple oxidants (*e.g.* Fe^{III} ions and complexes), the emphasis was on the nature of the intermediate species formed in going from N_2H_4 to N_2 and NH_3 .³⁻⁶ In the case of oxidants which undergo a change in oxidation number of two or more, the oxidant species involved have also been studied. In the particular case of Cr^{VI} , the current view recognizes the following reactions



as the first stage. The details of the fast reactions of Cr^{IV} and N_2H_2 to give Cr^{III} and N_2 have been reported and involve the reactions



The analysis of Haight *et al.*¹¹ suggests that the reactions



are the most likely.

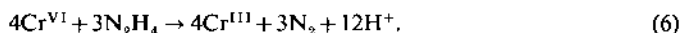
We are currently exploring the mechanism of heterogeneous oxidation of hydrazine and we present here the results of a study of the oxidation of hydrazine by an aqueous suspension of barium chromate; we shall report separately a study of the reaction of hydrazine with iron(III) oxides. As our main interest is the extent to which heterogeneity affects the reaction rate, our discussion is centred on a comparison of the oxidation of hydrazine by $Cr^{VI}(aq)$ and by $Cr^{VI}(solid)$.

Heterogeneous oxidation has recently become a valuable tool in organic chemistry. Solid permanganate salts have been shown to exhibit remarkable selectivity for the oxidation of alcohols in aprotic solvents.^{12, 13} The mechanisms remain highly speculative but certainly involve binding of substrate molecules with reactive sites on the solid surface. This is also true for the oxidation of hydrazine by barium chromate in aqueous suspensions.

EXPERIMENTAL

The kinetics of the reaction was followed by measuring the pressure exerted by the nitrogen formed at constant volume as a function of time using the apparatus depicted schematically in fig. 1. Appropriate amounts of barium chromate were suspended in 85 cm³ of a sodium acetate + acetic acid buffer (pH 4.7). This suspension, contained in reaction flask A, was thermostatted at 30 °C by water circulating through a jacket and stirred magnetically for at least 1 h, as this was the minimum time required to saturate with acetic acid vapour the space above the liquid in flasks A and C and the connecting tube. In order to achieve the initial equilibrium, stopcock D was opened and closed quickly until no further increase in the pressure of the system was detected. To start the reaction, N_2H_4 was poured from the thermostatted tube B into the reaction flask. As nitrogen was produced by the oxidation reaction, pressure was exerted on the manometric liquid in flask C (coloured water) and its magnitude was read on scale E. The volume, or more specifically the cross-section, of flask C was chosen in such a way that the error produced by the transfer of the liquid from flask C to the manometric tube F was minimized. Thus, the initial level in tube F was considered to be constant throughout the reaction. This constant-volume method proved to be superior to the classical gas-burette method, in which the gas volume is measured at constant pressure by adjusting the liquid level and changing the height of the burette. It was found that this procedure gave unreliable results in our case, especially at the beginning of the reaction when nitrogen production was fast, because of fluctuations in the liquid level when changing the height of the burette.

Values of the measured pressures were plotted against time. In all cases an initial linear relationship was observed, typically up to 10–15% of the total extent of reaction, calculated from the stoichiometry given by⁷⁻¹¹



Beyond this point, the reaction slowed down considerably. In general, the final pressures observed after a reasonably long time corresponded to ca. 70% of the total reaction. No special effort was put into measuring the actual stoichiometry as several sources of error render this measurement difficult (nitrogen solubility, very slow approach to total conversion, poisoning of the dissolving solid surface *etc.*).

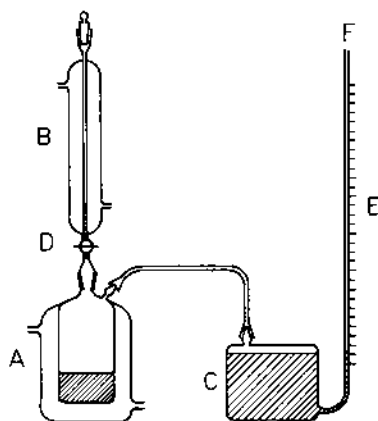


Fig. 1. Schematic diagram of the experimental apparatus.

The reaction rates were calculated from the initial slopes $\Delta p/\Delta t$ and expressed as $\Delta n/\Delta t$ (where n is number of moles of nitrogen produced) by multiplying by the factor V/RT (where V is the volume of the gaseous space in the reaction apparatus, 0.62 dm^3).

Barium chromate was precipitated by mixing a BaCl_2 solution, slightly acidified with acetic acid, with a K_2CrO_4 solution. For the present study, the fraction between 230 and 270 mesh (sieve opening between 6.2×10^{-6} and $5.3 \times 10^{-6} \text{ m}$) was used. Its specific surface area, obtained by nitrogen adsorption in a Micromeritics Accusorb B.E.T. apparatus, was $3.3 \text{ m}^2 \text{ g}^{-1}$.

Mobilities were determined at 30°C using a Carl Zeiss cytopherometer.

Stock hydrazine solutions were prepared by dilution of a concentrated AnalaR (B.D.H.) hydrazine solution. Its concentration was frequently checked by titration with standard iodate.

RESULTS AND DISCUSSION

Under our experimental conditions, the concentrations of CrO_4^{2-} and HCrO_4^- were calculated from solubility and protolytic data^{14,15} and found to be 7×10^{-7} and $1.08 \times 10^{-5} \text{ mol dm}^{-3}$, respectively. Hydrazine is *ca.* 100% in the form of N_2H_5^+ .⁷ Using the data obtained by Haight *et al.*,¹¹ the rate for the homogeneous oxidation of hydrazine under conditions typical of the heterogeneous reaction was calculated to be $2.9 \times 10^{-11} \text{ mol dm}^{-3} \text{ s}^{-1}$, whereas our experimental initial rate is $2.35 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$. The large acceleration indicates that a heterogeneous process is taking place.[†]

Measurements were performed at pH 4.7 because of experimental difficulties (a large BaCrO_4 solubility at lower pH values and low reaction rates at higher pH values, which are probably caused by the strong dependence of chemisorption on pH).¹⁸

Fig. 2 shows the dependence of initial reaction rate on the total mass of BaCrO_4 . As expected, the rate increased linearly with increasing available surface area; thus, the fraction adsorbed hydrazine/total hydrazine is low.

The adsorption of hydrazine onto barium chromate can be regarded in principle as being similar to the adsorption on binary or ternary oxides such as Fe_2O_3 or NiFe_2O_4 . Adsorption of simple amines onto oxides has been shown to be dependent upon the amine protolytic equilibrium, the charge on the oxide surface and the

[†] As pointed out by a referee, the reaction between N_2H_4 and MnO_2 leads eventually to MnOOH , without further reaction,¹⁶ whereas the homogeneous reduction of N_2H_4 by Mn^{II} is fast.¹⁷ This indicates that in this case the effect of the surface is the reverse of what has been observed by us.

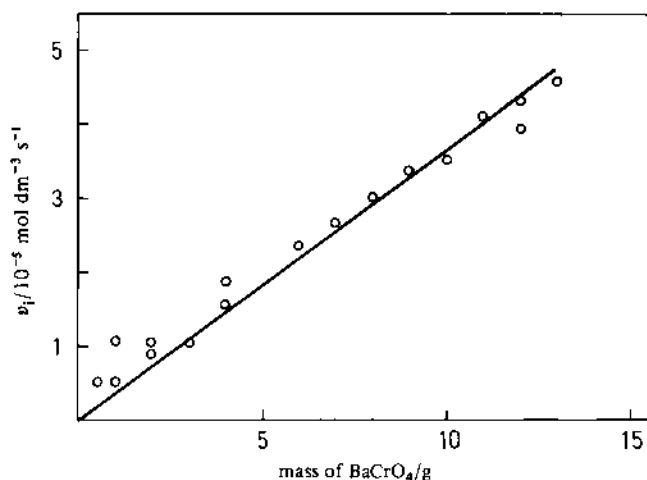


Fig. 2. Initial reaction rate, v_i , as a function of the mass of $BaCrO_4$. pH 4.7, temperature 30 °C, $[N_2H_4] = 8.7 \times 10^{-3} \text{ mol dm}^{-3}$.

chemical affinity between the substrate and the solid.^{19, 20} In the case of barium chromate, the charge on the surface is determined both by the concentration of CrO_4^{2-} and Ba^{2+} ions (*cf. e.g.* AgI ^{21, 22}) and by the concentration of H^+ ions (*cf. e.g.* Fe_3O_4 ^{23, 24}). We measured the electrophoretic mobilities of $BaCrO_4$ in our suspensions and the results show that at pH 4.7 (acetic acid+acetate) and ionic strength $I = 10^{-3} \text{ mol dm}^{-3}$, ζ (zeta potential) is slightly negative, $\zeta = -20 \text{ mV}$, and approaches zero as the ionic strength increases. Thus, electrostatic interactions alone would not lead to appreciable adsorption of $N_2H_4^+$, which must be regarded as essentially chemical in nature. The Gibbs energy for the chemisorption of complexing molecules or ions onto metal oxides is related to the corresponding Gibbs energy in homogeneous solutions.^{18, 25} In the present case, complexation in solution is known to take place with formation of $Cr^{VI}-NH-NH_2$ species;^{7, 9} we therefore propose the following chemisorption equilibrium for the heterogeneous case:



where $-Cr-OH$ is the Cr-containing part of the surface, as a first, fast pre-equilibrium for the oxidation reaction [adsorption/desorption processes are fast, and they cannot control the rate; this must also be true for the analogous adduct formation, thus making kinetic control of forward reaction (1), as postulated by Gupta *et al.*,⁷ unlikely]. The occurrence of reaction (7) as an adsorption equilibrium is borne out by the dependence of the rate on hydrazine concentration, which shows behaviour typical of an adsorption isotherm of the Langmuir type:

$$v_i = kK_L[N_2H_4]_{aq}/(K_L[N_2H_4]_{aq} + 1) \quad (8)$$

where v_i is the initial rate of reaction, k is the rate constant corresponding to the decomposition of the adsorption complex and K_L is the adsorption equilibrium constant [corresponding to reaction (7)]. When v_i^{-1} is plotted against $[N_2H_4]_{aq}^{-1}$ (fig. 3) a straight line is obtained, thus demonstrating the applicability of eqn (8) to our results. From the slope and the intercept, the following values were obtained: $k = 5.7 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ and $K_L = 1.14 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$. The relatively low affinity

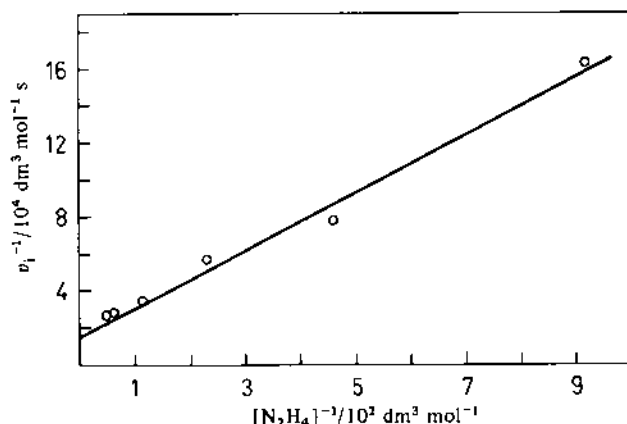


Fig. 3. Reciprocal plot corresponding to eqn (8). pH 4.7, temperature 30 °C, mass of BaCrO_4 8 g.

of hydrazine for the BaCrO_4 surface, shown by this low K_L value, and the lack of saturation even at $2 \times 10^{-2} \text{ mol dm}^{-3} \text{ N}_2\text{H}_4$ are in good agreement with the value reported for the equivalent homogeneous equilibrium ($K_1 = 3.2 \text{ dm}^3 \text{ mol}^{-1}$) between CrO_4H^- and N_2H_5^+ .¹¹

Note that a dissociative adsorption, *i.e.*



at very low coverages also agrees with our data, as can be seen in fig. 4, where the initial rates have been plotted against $[\text{N}_2\text{H}_4]^{\frac{1}{2}}$. However, it seems unlikely that the acceleratory effect is due to dissociative adsorption. It has been shown that the mechanism of the anodical oxidation of hydrazine does not involve the breakage of N—N bonds; even when ammonia is formed, it is not from NH_2 radicals but from the decomposition of N_4H_4 .^{26, 28}

The acceleration found for the heterogeneous reaction compared with the homogeneous one can be traced back to the increased concentration of the adduct and/or its increased reactivity. The concentration of the adsorption complex can be calculated from

$$[-\text{Cr}-\text{NH}_2-\text{NH}_2] = K_L(1-\theta) N_s A m [\text{N}_2\text{H}_4] / V N \quad (10)$$

where θ is the fraction of occupied sites, N_s is the number of reactive sites, A is the specific surface area, m is the mass of BaCrO_4 , V is the volume of the suspension and N is Avogadro's number. At a hydrazine concentration of $1 \times 10^{-2} \text{ mol dm}^{-3}$ and a coverage θ of 0.52, a value of $2.7 \times 10^{-3} \text{ mol dm}^{-3}$ is obtained for $[-\text{Cr}-\text{NH}_2-\text{NH}_2]$. In the calculation a value of $1 \times 10^{13} \text{ sites cm}^{-2}$ has been used for N_s , as estimated from crystallographic data²⁹ using the assumption that all four chromium atoms in a unit cell lie on the same plane. This is probably an overestimation, and so the concentration of the adsorption complex, as calculated in this way, should be considered as an upper limit. For m and V , the experimental values of 8 g and 0.085 dm^3 have been used. For the parallel homogeneous reaction under similar conditions, $[\text{N}_2\text{H}_4\text{CrO}_3] = K[\text{HCrO}_4^-][\text{N}_2\text{H}_5^+] = 3.5 \times 10^{-7} \text{ mol dm}^{-3}$ is obtained. This indicates that there is an increase in the concentration of the reactive species in the heterogeneous reaction as compared with the homogeneous reaction by a factor

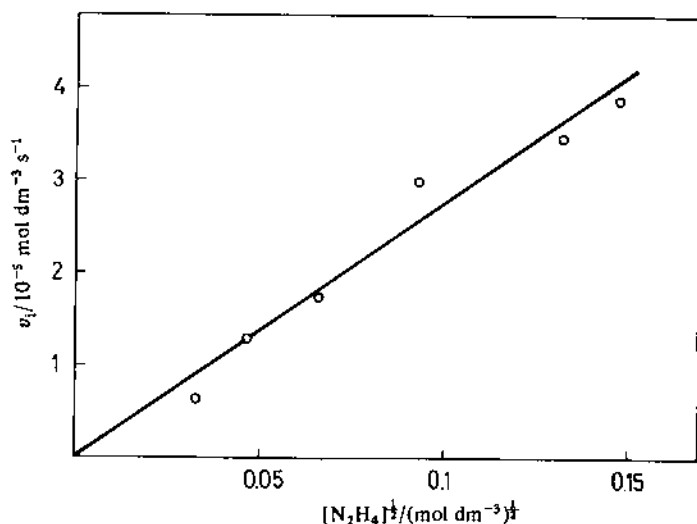


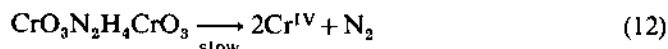
Fig. 4. Dependence of the initial reaction rate, v_i , on $[N_2H_4]^{1/2}$. pH 4.7, temperature 30 °C, mass of $BaCrO_4$ 8 g.

of 7.7×10^3 . The difference between this value and the actual acceleration factor, *ca.* 10^6 , has to be ascribed to differences in the k values [reaction (2)]. Haight *et al.*¹¹ reported $k_{hom} = 1.1 \times 10^{-4}\ s^{-1}$ at pH 4.7, whilst our data indicate that $k_{het} = 5.7 \times 10^{-8}\ dm^3\ mol^{-1}\ s^{-1}$, which can be converted into $k'_{het} = 1.1 \times 10^{-2}\ s^{-1}$ by taking into consideration N_s , A , m and V . Thus, the heterogeneous adduct is at least one hundred times more reactive than the homogeneous complex. Note that our calculations yield the upper limit for the intermediate concentration, so that the decomposition rate enhancement factor of 10^3 is in fact a lower limit.

It is tempting to conclude that neighbouring Cr^{VI} centres play an active role in the decomposition of the adduct, in a manner similar to that proposed by Beck and Durham⁹ for the reaction in homogeneous solution:



This diester decomposes slowly



thus providing another pathway which might increase the overall reaction rate.

We thank Lic. J. Lesk for collaborating during the early stages of this research and J. Helzel García for useful suggestions concerning the experimental procedure.

¹ L. F. Audrieth and B. A. Ogg, *The Chemistry of Hydrazine* (Wiley, New York, 1951).

² F. Bottomley, *Q. Rev.*, 1970, **24**, 617.

³ J. W. Cahn and R. E. Powell, *J. Am. Chem. Soc.*, 1954, **76**, 2568.

⁴ W. C. E. Higginson and P. Wright, *J. Chem. Soc.*, 1955, 1551.

⁵ D. R. Rosseinsky, *J. Chem. Soc.*, 1957, 4685.

⁶ H. Minato, E. J. Meehan, I. M. Kolthoff and C. Auerbach, *J. Am. Chem. Soc.*, 1959, **81**, 6168.

⁷ K. K. Sen Gupta, S. S. Gupta and H. R. Chatterjee, *J. Inorg. Nucl. Chem.*, 1976, **38**, 549.

⁸ V. M. S. Ramanujam, S. Sundaram and N. Venkatasubramanian, *Inorg. Chim. Acta*, 1975, **13**, 133.

- ⁹ M. T. Beck and D. A. Durham, *J. Inorg. Nucl. Chem.*, 1970, **32**, 1971.
- ¹⁰ G. P. Haight Jr, T. J. Huang and B. Z. Shakhshiri, *J. Inorg. Nucl. Chem.*, 1971, **33**, 2169.
- ¹¹ G. P. Haight Jr, T. J. Huang and H. Platt, *J. Am. Chem. Soc.*, 1974, **96**, 3137.
- ¹² N. A. Noureldin and D. G. Lee, *Tetrahedron Lett.*, 1981, 4889.
- ¹³ D. G. Lee and N. A. Noureldin, *J. Am. Chem. Soc.*, 1983, **105**, 3188.
- ¹⁴ A. Seidell and W. F. Linke, *Solubilities of Inorganic and Metal Organic Compounds* (American Chemical Society, Washington, D.C., 1958).
- ¹⁵ A. E. Martell and R. M. Smith, *Critical Stability Constants* (Plenum Press, New York, 1977).
- ¹⁶ W. C. Maskell, J. E. A. Shaw and F. L. Tye, *Electrochim. Acta*, 1981, **26**, 1403.
- ¹⁷ G. Davies and K. Kustin, *J. Phys. Chem.*, 1969, **73**, 2248.
- ¹⁸ M. A. Blesa, E. Borghi, A. J. G. Maroto and A. E. Regazzoni, *J. Colloid Interface Sci.*, 1984, **98**, 295.
- ¹⁹ S. L. Swartzen-Allen and E. Matijević, *Chem. Rev.*, 1974, **74**, 385.
- ²⁰ S. G. de Buseti, E. A. Ferreira and A. K. Helmi, *Clays Clay Miner.*, 1980, **28**, 149.
- ²¹ P. C. Hiemenz, *Principles of Colloid and Surface Chemistry* (Marcel Dekker, New York, 1977).
- ²² *Colloid Science*, ed. H. R. Kruyt (Elsevier, New York, 1949).
- ²³ A. E. Regazzoni, M. A. Blesa and A. J. G. Maroto, *J. Colloid Interface Sci.*, 1983, **91**, 560.
- ²⁴ A. E. Regazzoni, N. M. Figliolia, M. A. Blesa and A. J. G. Maroto, *J. Colloid Interface Sci.*, 1984, **101**, 410.
- ²⁵ L. Sigg and W. Stumm, *Colloid Surf.*, 1980, **2**, 101.
- ²⁶ K. Arnolds, J. Heitbaum and W. Vielstich, *Z. Naturforsch., Teil A*, 1974, **29**, 359.
- ²⁷ S. Karp and L. Meites, *J. Am. Chem. Soc.*, 1962, **84**, 906.
- ²⁸ Y. Fukumoto, T. Matsunaga and T. Hayashi, *Electrochim. Acta*, 1981, **26**, 631.
- ²⁹ C. W. Pistorius and M. C. Pistorius, *Z. Kristallogr.*, 1962, **117**, 259.