

the method does not suffer from the interference of starch, talc, lactose, sucrose and gum which are used in tablet. The values of molar absorptivity indicate that all the reagents are equally sensitive. The proposed method can be used satisfactorily in routine quality control analysis of chlorcyclizine hydrochloride.

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EVALUATION OF TRUE RATE CONSTANTS FOR THE CATALYTIC DECOMPOSITION OF NITROUS OXIDE—A GENERAL NUMERICAL METHOD

PRODUCT inhibition is a common phenomenon observed in heterogeneous catalysis. In a number of instances, the experimental parameter (concentration) used to evaluate the rate constants is found to be affected due to considerable retention of the products on the surface. In the typical test reaction like N_2O decomposition studied by the authors over a series of solid solutions of LaMnO_3 — SrMnO_3 , the rate constants evaluated through the measurement of pressure changes as a function of time were found to be lower due to the retention of the product oxygen on the surface. Usually the plots of the relevant kinetic data vs time gave intercepts on the time axis which should not be observed if there were no simultaneous adsorption. In the present communication, a procedure has been described to overcome this discrepancy in the analysis of kinetic data.

At an initial pressure of 200 torr, the mechanism of N_2O decomposition involved oxygen desorption to be the rate determining step¹ and the kinetics obeyed the rate equation²

$$-\frac{dP_{\text{N}_2\text{O}}}{dt} = \frac{kP_{\text{N}_2\text{O}}}{(P_{\text{O}_2})^{\frac{1}{2}}} \quad (1)$$

where $P_{\text{N}_2\text{O}}$ and P_{O_2} are the pressures of N_2O and O_2 at time t respectively. The integrated form of this equation is

$$\frac{P_{\text{O}_2}^{\frac{1}{2}}}{\sqrt{2}} \ln \frac{P_{\text{O}_2}^{\frac{1}{2}} + x^{\frac{1}{2}}}{P_{\text{O}_2}^{\frac{1}{2}} - x^{\frac{1}{2}}} - \sqrt{2}x^{\frac{1}{2}} = kt \quad (2)$$

where P_0 is the initial pressure of N_2O and x is the pressure of N_2O decomposed at the time t . Values of k were usually calculated from the slope of a plot of L.H.S. of equation (2) against time. The reaction was usually followed for a period of one hour and the temperatures of the reaction were so chosen that the percentage of decomposition was always less than 20% in one hour.

When the plots were made with the experimental data, it was observed that there was no linearity in the initial stages of the reaction (i.e., points during the initial 5 minutes). This has also been observed in a number of cases reported in literature³⁻⁴. A least square analysis of the experimental data according to equation (2) also gave a definite intercept whereas in an ideal situation the intercept should be equal to zero. Moreover, the intercept was found to be temperature dependent. Cimino *et al.*² have observed an induction time for N_2O decomposition implying that all the oxygen produced has been retained by the catalyst. However, it is probable that in many of the cases, oxygen retention by the catalyst can be only fractional which has also been experimentally verified in our studies on $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and rare earth manganite systems. This was deduced from the observation that there was definite increase of pressure at intervals less than the intercept time calculated by the least square analysis. It is therefore concluded that the uptake of oxygen is a time dependent process till it reaches its equilibrium surface coverage.

As a consequence of this uptake of oxygen produced during the decomposition, the rate constants evaluated from the slopes of the plots would obviously be lower than those where there was no retention of oxygen. The true rate constants can be evaluated only after correcting the pressure values taking into account the oxygen retention at various time intervals. This has been achieved as follows. A plot of L.H.S. (equation 2) vs time was made. By least square regression method, the intercept on the time axis (t_0) was evaluated. Substituting this intercept time (t_0) in equation (2), the value of x was found out. The amount of oxygen retained would therefore be $(x/2)$ (half of N_2O decomposed). It has been observed that this quantity of oxygen has been taken up by the catalyst over a time interval t_1 (t_1 was evaluated by trial and error and found to vary between 2 and 10 minutes for the systems studied) wherein the adsorption rate itself obeyed a kinetic equation of the type⁵

$$\frac{x}{2} = \frac{1}{a} \ln \left(\frac{t_1 + t_0}{t_0} \right) \quad (3)$$

where a is a constant.

Thus the oxygen retention at various time intervals were evaluated and the corresponding pressure values

TABLE I

Values of kinetic parameters for N_2O decomposition on $La_{1-x}Sr_xMnO_3$ before and after correction for simultaneous oxygen retention

Catalyst	TK	before regression			intercept (minutes)	volume of oxygen added (ml)	after regression		
		rate constant ^a $\times 10^4$	E kcal/s mol^{-1}	$\ln A^b$			rate constant $\times 10^4$	E kcal/s mol^{-1}	$\ln A^b$
$x = 0$	290	2.39			4.74	0.20	2.65		
	300	3.47	18.9	8.67	3.44	0.22	3.83	18.2	8.08
	320	5.46			2.88	0.23	5.93		
	340	9.97			1.75	0.24	10.44		
$x = 0.3$	260	3.40			2.57	0.20	3.65		
	280	4.55	6.2	-2.08	2.10	0.23	4.90	7.2	-1.02
	300	5.12			1.44	0.26	5.90		
$x = 0.65$	260	1.66			3.57	0.13	1.83		
	280	3.03			2.71	0.18	3.44		
	305	6.57	18.0	8.47	2.11	0.23	7.27	18.0	8.49
	320	9.50			1.85	0.25	10.22		
	330	12.42			1.59	0.26	13.30		
$x = 1.0$	315	4.27			3.84	0.18	4.90		
	340	6.76	12.4	2.86	2.94	0.19	7.49	11.6	2.37
	360	8.36			2.83	0.21	9.11		
	380	12.78			2.15	0.23	13.80		

^aunits of rate constant $mm^{\frac{1}{2}} min^{-1}m^{-2}$.

^blogarithm of frequency factor.

were corrected so as to obtain a true estimate of the decomposition at any given time. A linear regression of L.H.S. (equation 2) with the newly corrected experimental data vs time now gave an intercept less than the one obtained initially. The regression was continued till the intercept was zero. The volumes of oxygen retained as calculated by this method at various temperatures on a few catalysts are given in Table I. The fact that the plots now pass through the origin shows that the parameters deduced from them can be considered to represent the kinetics of the actual decomposition process taking place on the surface irrespective of the amount of oxygen retained by the surface.

The results given in Table I indicate that :

1. The values of rate constants normally evaluated by applying equation (2) and using the raw

experimental data are 10-20% lower than the values of true rate constants.

2. It is seen that the use of either true rate constant or the apparent rate constant as evaluated from raw kinetic data does not alter the values of the Arrhenius parameters to any significant extent.

3. The procedure outlined can also be used to make an estimate of oxygen retention on the catalyst. The saturation values of oxygen adsorption on $LaMnO_3$ at 280°C, 320°C and 360°C were found to be 0.10 ml, 0.20 ml and 0.32 ml respectively. It will be seen that the oxygen retention by the catalyst is comparable to the amount of oxygen adsorption evaluated by independent adsorption measurements.

The award of a teacher fellowship to one of the authors (S. L. R.) by the University Grants Commission, New Delhi, is gratefully acknowledged.

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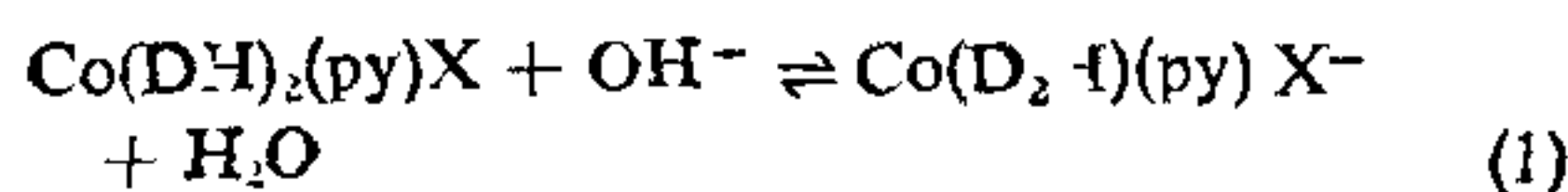
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DEPROTONATION CONSTANTS OF SOME TRANS-ACIDOPYRIDINEBIS(DIMETHYL- GLYOXIMATO)COBALT(III) COMPLEXES

It has been observed that the addition of alkali to solutions of *trans*-bis(dimethylglyoximate)cobalt(III) complexes results in a rapid and reversible change in the visible and near uv-region, attributable to the reversible loss of a bridging proton by the dimethylglyoxime ligands¹⁻⁴. The effect of various groups on the ease of dissociation of this proton can be measured in terms of the proton dissociation constant, thus providing a direct measure of the electronic transmission in these complexes. In this note, we report the results of our studies on the deprotonation equilibrium constants of the following complexes; *trans*-Co(DH)₂(py)I, *trans*-Co(DH)₂(py)NCS, and *trans*-Co(DH)₂(py)NO₂. Also, we reinvestigated the complexes, *trans*-Co(DH)₂(py)Br, *trans*-Co(DH)₂(py)Cl and *trans*-Co(DH)₂(py)N₃ (where DH⁻ = dimethylglyoximate anion) under the present experimental conditions.

All the complexes were prepared as reported in the literature^{5,6}.

The equilibrium may be represented as



where the deprotonation constant K is given by

$$K = \frac{[\text{Co(DH)}(\text{py})\text{X}^-][\text{OH}^-]}{[\text{Co(DH)}_2(\text{py})\text{X}]} \quad (2)$$

Values of K were determined spectrophotometrically at 370 nm for Co(DH)₂(py)I and at 400 nm for all

the other complexes in aqueous dimethylsulphoxide (10% v/v) and at an ionic strength 1.0 M (NaNO₃). The values are shown in Table I. These constants are a useful measure of the acidity of the hydrogen bonded proton and the trend in their values may be explained on the basis of the electronic transmission in these systems. The following is the order of increasing K values I⁻ ~ Br⁻ < Cl⁻ ~ N₃⁻ < NCS⁻ < NO₂⁻

TABLE I

Deprotonation constants of some *trans*-acidopyridinebis(dimethylglyoximate)cobalt(III) complexes

Temp. = 27.0° C, Solvent = aq. DMSO (10% v/v);
I = 1.0 M (NaNO₃)

Complex	K (M ⁻¹)
Co(DH) ₂ (py)I	1023 ± 40
Co(DH) ₂ (py)Br	1098 ± 85
Co(DH) ₂ (py)Cl	1664 ± 590
Co(DH) ₂ (py)N ₃	1970 ± 319
Co(DH) ₂ (py)NCS	3198 ± 876
Co(DH) ₂ (py)NO ₂	6033 ± 1678

The greater acid-strengthening effect of the unsaturated ligands N₃⁻, NCS⁻ and NO₂⁻ can be explained on the basis of their electron withdrawal nature via the π-system of electrons from the ligand bound to the metal. Metal-ligand π-charge transfer from the filled d_{xy} or d_{yz} metal orbitals to the lowest unoccupied π* orbital on these ligands would reduce the electron density on the metal. This would enhance the Co-N bond strength because of a higher demand of the metal for the lone pair of the equatorial nitrogen resulting in turn in a stronger N-O bond and a weaker O-H bond, leading to greater acidity.

The coordinated halide ions increase the electron-density on the cobalt by inductive effects through the sigma bond systems, thereby decreasing the demand of the metal for the lone pair of the equatorial nitrogen of DH resulting in a weaker N-O bond, and stronger O-H bond, decreasing the acidity. From the results, it is seen that the deprotonation constants are not very sensitive to variation of halogens.

One of the authors (P.N.B.) acknowledges the award of a junior research fellowship from the Special