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KINETICS OF THE ADDITION OF KETONES WITH 2,4-DINITROPHENYLHYDRAZINE

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THE addition of ketone with hydrazine is well known[1], but studies of kinetics of such reactions are very few[2] due to the rapidity of the reactions. The kinetics of the addition of acetone and ethylmethylketone, with 2,4-dinitrophenylhydrazine (DNPH) in aqueous acidic medium have therefore been studied for evaluating the kinetic parameters.

The reactions were comparatively fast and not amenable to conventional technique and hence a polarographic method was adopted[3,4]. This was possible because DNPH yields diffusion current at DME while acetone, ethylmethylketone and the product which precipitates out do not significantly do so.

Equimolar concentrations of the ketone and DNPH in 0.3 M sulphuric acid were mixed and the change in concentration of DNPH was followed from its diffusion current. Care was taken to presaturate the reaction system with the addition product so that the change in diffusion current with time truly represented the kinetics of the addition reaction. The concentration of unreacted DNPH at various time intervals during the reaction was estimated from a calibration curve obtained by measuring the galvanometer deflections with known concentrations of DNPH in the solution presaturated with the addition product. The DME was adjusted to yield precisely 24 drops per minute and the diffusion current at every fourth drop (*i.e.* interval of 10 sec) was recorded. From the readings (table 1) 1/[DNPH] versus time was plotted and the curve was linear indicating that the reaction was of the second order[5]. The slope of the curve evaluated by least square analysis showed a specific reaction rate. The kinetic studies with non-equimolar concentrations of the reactants confirmed these findings. Repeated trials yielded results agreeing to within 3%. Similar studies were carried out at various temperatures and the activation parameters were evaluated. The effect of acidity and solvent composition on the specific rate was also investigated.

Table 1 *The kinetics of addition of acetone and DNPH in 0.3 M sulphuric acid*

Time (t/sec)	Deflection (d/cm)	Conc. of unreacted DNPH/10^{-3} M	$\frac{1}{\text{DNPH}}/10^2\ \text{M}^{-1}$
0	21.9	3.00	3.33
20	20.5	2.81	3.56
30	19.8	2.71	3.69
40	19.3	2.64	3.78
50	18.7	2.56	3.90
60	18.2	2.49	4.01
70	17.7	2.42	4.12
80	17.2	2.36	4.24
90	16.8	2.30	4.34
100	16.3	2.23	4.48
120	15.5	2.12	4.71
140	14.8	2.02	4.94
160	14.1	1.93	5.18
180	13.5	1.85	5.40
240	12.0	1.64	6.09

Initial concentration of acetone and DNPH: 3.0×10^{-3} M; ionic strength of the reaction medium: 4.2×10^{-1} M; temperature: 25°C

Table 2 *Kinetic parameters of addition of acetone/ethylmethylketone and DNPH*

	Specific rate at 25.0°C ($k_2/M^{-1}\,Sec^{-1}$)	Energy of activation (E_a/kJ mol^{-1})	Frequency factor ($A/M^{-1}\,Sec^{-1}$)	Entropy of activation $\Delta S/JK^{-1}\,mol^{-1}$
Acetone	1.13	13.3	2.42×10^2	−207
Ethylmethylketone	2.83	46.8	4.52×10^8	− 87.5

Table 3 *Effect of acidity on the specific rate of the addition of acetone and DNPH*

Concentration of sulphuric acid/M	0.30	0.45	0.54	0.60	0.66	0.75
$k_2/M^{-1}\,Sec^{-1}$	1.13	0.51	0.36	0.27	0.22	0.15

Table 4 *Solvent effect on the specific rate of the addition of acetone and DNPH*

Percentage of 1,4 dioxane/%	0.0	5.0	7.5	10.0	15.0	20.0
$k_2/M^{-1}\,Sec^{-1}$	1.13	0.95	0.88	0.83	0.73	0.57

The various activation parameters evaluated are presented in table 2. The specific rate and the activation energy values in ethylmethylketone are higher than those in acetone. With increase in acidity the specific rate decreases (table 3). Similarly the specific rate decreases with increase in the percentage of dioxane (table 4).

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TWO DIMENSIONAL ELECTROPHORETIC DETECTION OF ABNORMAL SERUM PROTEIN IN PATIENTS WITH ENDOMYOCARDIAL FIBROSIS

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ENDOMYOCARDIAL fibrosis[1] (EMF) is one of the common causes of heart failure in the tropical world. It is an endemic disease in Kerala when compared to other parts of India and nearly 10% of all the cardiovascular cases in children admitted to hospitals in Kerala State are found to be EMF[2]. Geld *et al*[3] have reported the occurrence of antimyocardial antibodies in patients with EMF and this prompted us to analyse the serum proteins of these patients by high resolution two-dimensional (2-D) electrophoresis on polyacrylamide gel. Our study has yielded meaningful data regarding the abnormalities in the serum proteins of EMF patients and provided an approach for developing a tool for the diagnosis of the disease.

Twenty patients angiographically confirmed to be suffering from EMF were taken for this study. An equal number of age and sex matched controls were selected from the apparently healthy donors who came to the blood bank of our hospital. Sera separated from the blood samples collected from the patients and controls were used for electrophoresis immediately.

The electrophoretic procedure was described by few workers[4,5]. For the first dimension, 4.75%, 2% cross-linked, polyacrylamide gel cast in Corning tubes of length 9.5 cm and internal diameter 2 mm were used. An aliquot (10 μl) of the serum was loaded on each tube and the electrophoresis was carried out using trisglycine buffer, pH 8.3, at a constant current of 1.2 mA per tube until the tracking dye (bromophenol blue) reached the 1 cm mark above the anode end of the tube. For the electrophoresis in the second dimension a 2–30% linear gradient gel slab was cast in a mould of