Mechanism of Addition of Methanol to Mestilyiminopropadienone†

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The addition of methanol to the mesityliminopropadienone compound **A** were studied by using ^{1}H NMR spectra which shows a complicated kinetics involving a fast reaction to about 35 % consumption followed by slow one. Consideration of the kinetics behaviours under different experimental conditions at 10 ºC and the product assignment provide valuable mechanistic insight into the system studied. The stoichiometry was observed to be 1:1 in terms of mesityliminopropadienone and methanol consumed and therefore, the overall order for the reaction is second order and the product formed was malonic ester amide (malonamate) **D**.

Key Words: Methanol, Mestilyiminopropadiene, Addition, Mechanism.

INTRODUCTION

The iminopropadienones, $RN{=}C{=}C{=}C{=}O$, constitute a recently discovered class of compounds[1]. While the simple alkyl derivatives (methyl[1], isopropyl[2] and *tert*- butyl[2]) are unstable compounds, which can, however, be isolated and characterized in low temperature matrices, the aryl derivatives are more stable and undergo chemical reactions, often in good preparative yields, under controlled conditions at temperatures around-100 to -50 ºC[3-7].

Several iminopropadienones are stable at room temperature, namely the mesityl[8], neopentyl[9] and *o-tert*-butylphenyl[9] derivatives.

In this paper, the kinetics of the addition reaction of methanol to the mesityliminopropadienones **A** which was generated from Meldrum's acid derivatives (5-[(disubsitituted) methylene]-2,2 dimethyl-3,5-dioxane-4,6-diones **B** and **C**) has been discussed.

Literature survey revealed that many studies were conducted regarding the addition of methanol to several alkenes[10-15] clearly explained, since mestyliminopropadienone are less stable so our attempt was made.

EXPERIMENTAL

Standard procedure for synthesis and preparative trapping of mesityliminopropadienone (A): 5-[(Mesityl-amino)(dimethylamine)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**C**) (332 mg, 1 mmol) was thermolyzed at 700 ºC under a vacuum of 10^{-4} mbar over 4 h, using an ice cooled U-tube as a cold trap. Upon completion of the thermolysis, the apparatus was flushed with N_2 and an excess or 1 eq of trapping agent in dilute solution (20 mL of dry THF or CH_2Cl_2) was injected through a septum onto the pyrolysate. After standing for a further 30 min in the ice, the U-tube was allowed to warm to room temperature and the solvent removed by rotary evaporation. The following compounds were isolated.

Mesityliminopropadienone (**A**) was first observed by Moloney[2] who generated it from the Meldrum's acid derivatives (**B**) and (**C**).
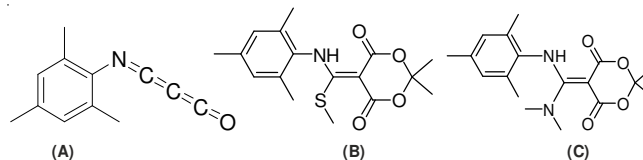
Meldrum's acid derivatives: Mesityliminopropadienone (**A**) was characterized by by IR spectroscopy and by chemical trapping with simple nuecleophiles[2].

All the reagents acetone, malonic acid CS_2 methylene diamine and 2,4,6-trimethyl aniline were of analytical grade, purified and distilled as given in the literature[16]. And the reaction was monitored by ^{1}H NMR using AV-400 FT-NMR spectrometer using the appropriate solvent signal for internal referencing.

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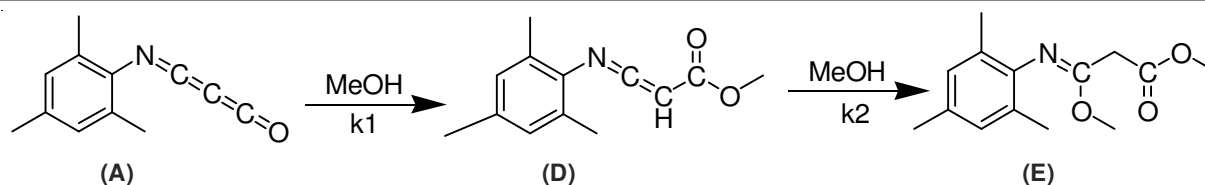
Scheme-I: Formation of malonic ester amide (E)

Kinetic measurement: 5-[(Mesitylamino)(methylthio) methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**B**) 300 mg (0.9 mmol), was thermolyzed at 700 ºC under a vacuum of 10^{-4} mbar over 4 h (assuming a maximum yield of 70 %, this would produce 0.63 mmol of pure iminopropadienone (**A**). The iminopropadienone formed was trapped onto a cold finger cooled with ice. Upon completion of the pyrolysis, the cold finger was allowed to warm up to 0 ºC and 1 mL of $CDCl_3$ was used to wash the material on the cold finger into the NMR tube that was connected to the shroud underneath the cold finger. 0.02 g (0.63 mmol) of pure methanol was added with a micro-syringe in the NMR tube just after the acquisition of the spectrum of the mesityliminopropadienone. The peak integrals as a function of time are given.

Product analysis: The mesityliminopropadienone, was mixed with methanol in the ratio of 1:1 under kinetics conditions and the reactions, which we presume would take place through two consecutive reactions in which the ketenimine (**D**) is formed first, followed by addition of the second molecule of methanol to afford the malonic ester amide (**E**), as shown in **Scheme-I**. The ratio of iminopropadienone (**A**) to methanol was *ca* 1:1, the reaction was monitored by ^{1}H NMR at 10 ºC for 665 min by integration of the aromatic protons of the iminopropadienone (**A**).

We could observe the formation of compound (**E**) by the appearance of two new signals simultaneously at 3.66 and 3.91 ppm, which were assigned to the two methoxy groups (Fig. 1). Another two peaks for compound (**E**) started to appear at 3.50 ppm (CH_2) and at 6.71 ppm, these two signals are in fact due to E[2,5]. It was difficult to separate the two signals of the aryl-CH_3 groups of the starting material (**A**) from those of the product (**E**), they appeared at 2.00 ppm and 2.21 ppm.

RESULTS AND DISCUSSION

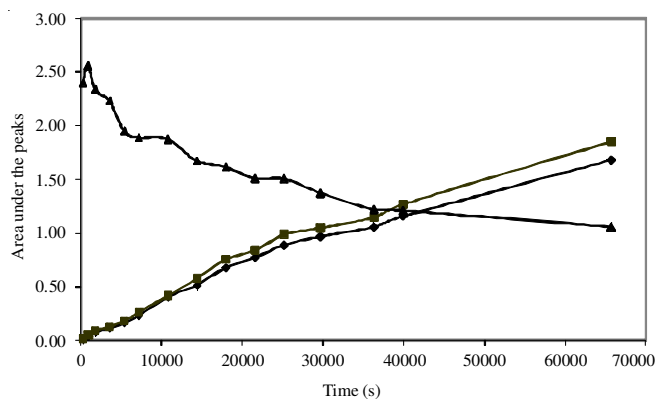The reaction was carried out under kinetics conditions that is the mesitylimimoprpadienone and methanol in the ratio of 1:1. The product of the reaction was malonic ester[2,5], the reaction was slow in the first step and which becoming faster in the second step so therefore, in order to take full advantage of the role of methanol concentration and temperature must be optimized. The addition of methanol to iminopropadienone has been studied kinetically as a function of [Mestyliminopropadienone] and [MeOH]. The results are compiled in Table-1 and Fig. 1, the proposed mechanism were shown in **Scheme-II**.

The starting material (A) (6.86 ppm) falls to about half in the first 10000 s, then falls much more slowly. We seem to have a fast initial reaction, consuming half of the starting

TABLE-1
TRAPPING OF MES-NC₃O WITH MeOH. INTEGRATION AREA FOR PEAKS AT 3.66, 3.91 AND 6.86 ppm

Time (s)	Peak at 3.66	Peak at 3.91	Peak at 6.86	ln [mes NC₃O]	1/[mes NC₃O]
0	0	0	4.23	1.442202	0.2364066
300	0.0122	0.0202	2.3998	0.8753854	0.4167014
900	0.0419	0.0502	2.5598	0.9399291	0.3906555
1800	0.0805	0.092	2.3379	0.8492531	0.4277343
3600	0.1163	0.1266	2.2313	0.8025844	0.4481692
5400	0.1656	0.1855	1.9485	0.6670598	0.5132153
7200	0.2376	0.2639	1.8900	0.6365768	0.5291005
10800	0.4084	0.4196	1.8753	0.6287686	0.533248
14400	0.5147	0.5766	1.6711	0.5134821	0.5984082
18000	0.6797	0.7575	1.6156	0.4797064	0.6189651
21600	0.7761	0.8415	1.5080	0.4107843	0.66313
25200	0.8886	0.9904	1.5061	0.4095235	0.6639665
29700	0.9694	1.0505	1.3729	0.3169253	0.7283852
36300	1.0582	1.1480	1.2221	0.2005707	0.8182636
39900	1.1576	1.2691	1.2123	0.1925194	0.8248783

Fig. 1. Plot areas under peaks: 3.66, 3.91 and 6.86 ppm
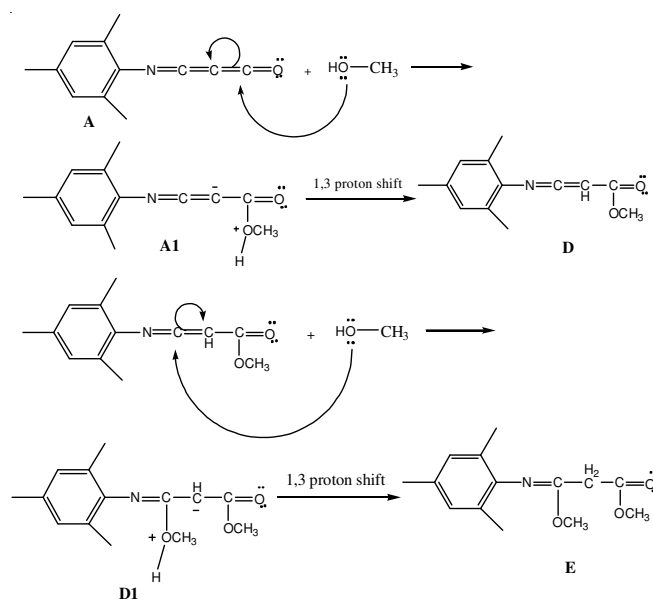
Scheme-II: Mechanism of addition of methanol to the mesityliminopropadienone

material (**A**), to form **D**, which indicated that we have a fast k1. The integrated decrease in the starting material (3*H*) should equal the increase in each CH_3 signal (3*H*) which indicate that we are may be measuring the reaction of **D** to **E** (slow k2).

Fig. 1 obtained by plotting of $\ln[mes\text{-}NC_3O]$ against the reaction time gave a curve (Fig. 2., $R^2 = 0.89$), on the other hand a plot of $1/[mes\text{-}NC_3O]$ against the reaction time gave straight line (Fig. 3), so the overall reaction order is second order. The rate equation is:
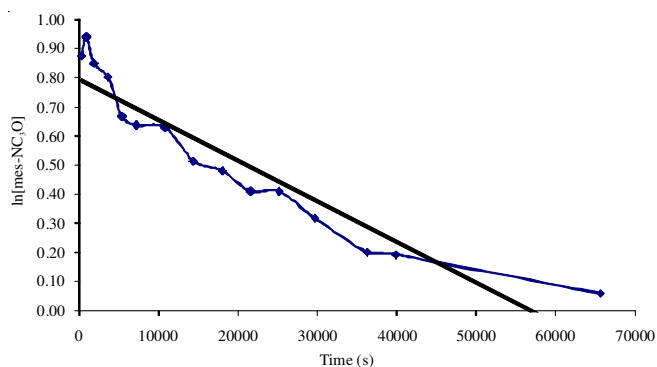
$$-d[mes\text{-}NC_3O]/dt = k_2[mes\text{-}NC_3O][MeOH]$$

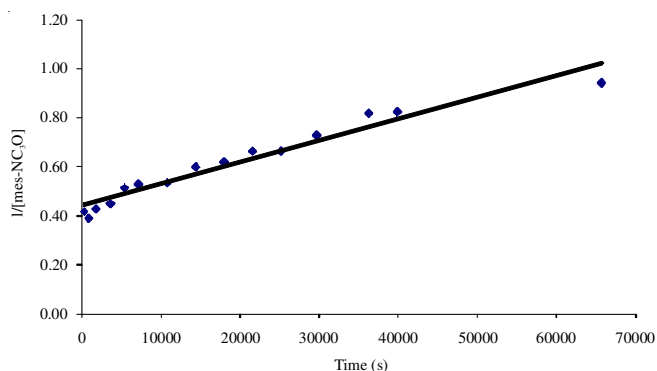Fig. 2. Plot of $\ln[mes\text{-}NC_3O]$ *vs.* reaction time ($R^2 = 0.89$)

Fig. 3. Plot of $1/[mes\text{-}NC_3O]$ *vs.* reaction time ($R^2 = 0.95$)

The linear fit obtained with (Microsoft Excel 2007), to get a slope of 9.0×10^{-6} (which is equal to the total reaction constant k) and an intercept of 0.4424 (which is equal to the reciprocal of the initial concentration of the mestylimino-propadienone (**A**)) with $R^2 = 0.95$.

The half life of the second order reaction (when the initial concentration of both reactants are equal) can be given by the equation $t_{1/2} = 1/k[mes\text{-}NC_3O]_0$, ($[mes\text{-}NC_3O]_0$ = the initial concentration of the iminopropadienone), so $t_{1/2}$ was found to be 49155 s (13 h and 39 min), which explains the fall-off of rate in Fig. 3, due to methanol being used up.

Reaction mechanism: Based on the result of our investigation under this condition used for the stiochiometry and kinetic studies, the reaction scheme with observed data proposed for the reaction is as below: The reactions would take place through two consecutive reactions *viz.*, step-1 in which the ketenimine (**D**) is formed first through the zwitterionic species **A1**[17], followed by the addition of the second molecule of methanol to afford the malonic ester amide (**E**) in step-2 through zwitterionic species **D1**, as shown in **Scheme-II**.

Conclusion

The absence of ^{1}H NMR evidence for intermediate for compound **D**, suggested that the first step is very fast and the second step is slow.

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