Monatshefte für Chemie 113, 941—948 (1982)

Monatshefte für Chemie
Chemical Monthly

Kinetics and Mechanism of Oxidation of Some Aliphatic Amines by Ditelluratocuprate(III)

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(Received 8 April 1981. Accepted 1 March 1982)

The kinetics of oxidation of some primary, secondary and tertiary aliphatic amines by ditelluratocuprate(III) was studied in alkaline medium. The order in both substrate and oxidant was found to be unity each. The reaction rate decreased with increase in ionic strength. The order of reactivity of amines was found to be secondary > primary > tertiary. A mechanism was proposed involving an adduct formation between amine and monotelluratocuprate(III), which dissociates further in a slow step followed by fast steps to give required products. The *Taft* linear free energy relationship was shown to be applicable which also supports the proposed mechanism.

[Keywords: Aliphatic amines; Cuprate(III); Taft relationship]

Kinetik und Mechanismus der Oxidation einiger aliphatischer Amine mit Kupfer(III)-ditellurat

Die Kinetik der Oxidation einiger primärer, sekundärer und tertiärer aliphatischer Amine mit Kupfer(III)-ditellurat wurde in alkalischem Medium untersucht. Die Reaktion war jeweils erster Ordnung bezüglich Substrat und Oxidationsmittel. Die Reaktionsgeschwindigkeit nahm mit zunehmender Ionenstärke ab. Die Reaktivität stieg in der Reihenfolge sekundäre > primäre > tertiäre Amine an. Ein Mechanismus, der die Bildung eines Adduktes zwischen Amin und Kupfer(III)-monotellurat beinhaltet, wird vorgeschlagen. Dieses Addukt dissoziiert in einem langsamen Schritt, gefolgt von schnellen Schritten, in denen die gefundenen Produkte gebildet werden. Die Anwendbarkeit der *Taft*-Beziehung wurde getestet und unterstützt den vorgeschlagenen Mechanismus.

0026-9247/82/0113/0941/$ 01.60

Introduction

The oxidations of amines by various oxidants like permanganate[1], lead tetraacetate[2], cobaltic perchlorate[3], chlorinedioxide[4], and *N*-bromosuccinimide[5] have been reported earlier. Systematic study on the kinetics of the oxidation of aliphatic amines by one-electron oxidants has received very little attention. In the oxidation of amines both α-hydrogen atom transfer and electron transfer from nitrogen can occur depending on the structure of amine, the oxidant etc. Hence the authors in continuation of their earlier work on the kinetics of oxidation of aliphatic alcohols[6], cyclic alcohols[7], aldehydes[8] using trivalent copper complexes, have taken up a systematic kinetic study of the oxidation of some primary, secondary and tertiary aliphatic amines to get a better understanding of the active form of trivalent copper, the role played by amine which is well known to form complexes with univalent and bivalent states of copper, as well as the other mechanistic details.

Experimental

Chemicals: All the chemicals used were of highest purity. Ditelluratocuprate (*DTC*) was prepared by the literature method[9].

Typical kinetic run: Substrate along with required amounts of KOH and K_2TeO_4 in the reaction flask and *DTC* solution in another flask were immersed in the thermostat at the desired temperature for one half hour before mixing. Nitrogen was bubbled through these solutions to expel dissolved oxygen. At required time intervals samples are taken and their absorbance was measured using a Carl-Zeiss-spectrophotometer at 405 nm. For fast reactions with half life times of the order of 5 minutes the kinetic runs at room temperature were followed by directly keeping the reaction mixture in the cuvet.

Results and Discussion

Under the conditions $[DTC] \ll [\text{amine}]$ the plot of log (A) vs. time (A is the absorbance of *DTC*) were linear indicating the order in $[DTC]$ to be unity (Fig. 1). From the slopes of linear plots obtained the pseudo first order rate constants k' were evaluated. The order in [amine] was one as obtained from the slope of the linear plot of log k' vs. log [amine]. Increase in $[OH^-]$ or [tellurate] decreased the rate of reaction at constant ionic strength (Fig. 1). The reaction rate decreased with increasing ionic strength of medium (Fig. 2). The *Debye-Hückel* plot of log k' vs. $\sqrt{\mu}$ gave a straight line with unit slope indicating that the reaction involves oppositely charged ions. Plots of $1/k'$ vs. $1/[\text{amine}]$ were linear passing through origin indicating the absence of any stable complex formation between the oxidant and substrate (Fig. 1). Stoi-

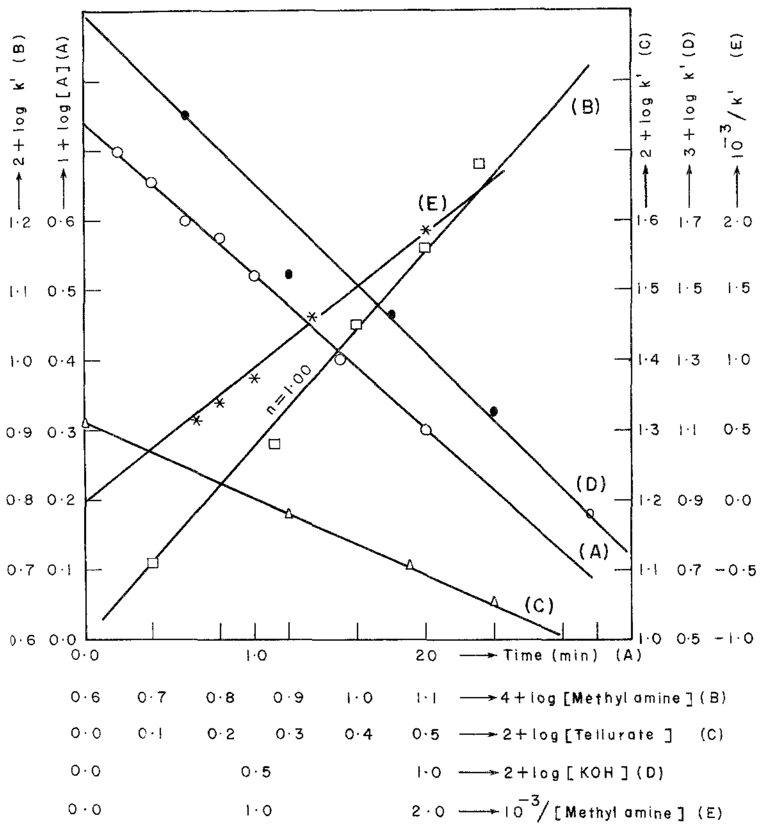

Fig. 1. *A* Order in [*DTC*]; *B* Order in [Methyl amine]; *C* Effect of [Tellurate] on rate of reaction; *D* Effect of [KOH] on rate of reaction; *E* Search for complex formation

chiometric studies indicated that two equivalents of oxidant are required for each mole of substrate consumed during oxidation. Ammonia and corresponding aldehyde or ketone were found to be the products of oxidation of aliphatic primary amines. In case of secondary or tertiary amines the products were found to be corresponding aldehyde and primary amine.

The inverse fractional order dependence on [tellurate] suggests that a dissociated species of *DTC* in which the Cu(III) moiety loses a tellurate ligand from the coordination sphere could be the active species in the reaction. This was postulated to be monotelluratocuprate(III) $\{Cu(OH)_2H_4TeO_6\}^-$ in our earlier publication[8]. A plausible mechanism proposed to explain the results is the following [monotelluratocuprate(III) is written as Cu(III)]:

$$\{Cu(OH)_2(H_4TeO_6)_2\}^{3-} + OH^- \overset{K_1}{\rightleftharpoons} \{Cu(OH)_2(H_4TeO_6)(H_3TeO_6)\}^{4-} + H_2O \quad (1)$$

$$\{Cu(OH)_2(H_4TeO_6)(H_3TeO_6)\}^{4-} \overset{K_2}{\rightleftharpoons} \{Cu(OH)_2(H_4TeO_6)\}^{-} + H_3TeO_6^{3-} \quad (2)$$

$$H_3TeO_6^{3-} + H_2O \overset{K_p}{\rightleftharpoons} H_4TeO_6^{2-} + OH^- \quad (3)$$

$$RCH_2NH_2 + H_2O \overset{K_h}{\rightleftharpoons} RCH_2NH_3^+ + OH^- \quad (4)$$

$$RCH_2NH_3^+ + Cu(III) \overset{K_3}{\rightleftharpoons} \text{adduct} \quad (5)$$

$$\text{adduct} \overset{\text{slow}}{\rightarrow} R\dot{C}HNH_2 + 2H^+ + Cu(II) \quad (6)$$

$$R\dot{C}HNH_2 + Cu(III) \overset{\text{fast}}{\rightarrow} RCH{=}NH + H^+ + Cu(II) \quad (7)$$

$$RCH{=}NH + H_2O \overset{\text{fast}}{\rightarrow} RCHO + NH_3 \quad (8)$$

The presence of free radicals is justified by the induced polymerization of acrylamide. The rate law for this mechanism comes out to be

$$\frac{-d[DTC]}{dt} = \frac{kK_1K_2K_3K_h[\{Cu(OH)_2(H_4TeO_6)_2\}^{3-}][RNH_2]\{K_p + [H_4TeO_6^{2}] + [OH^-]\}}{[OH^-][H_4TeO_6^{2-}]\{1 + K_1[OH^-]\}}$$

Prima facie it appears that RNH_3^+ may not be the active form of amine as the reactions are carried out in alkaline medium. But in these systems there is always a reversible equilibrium between protonated (RNH_3^+) and unprotonated forms (RNH_2) as represented by Eq. (4) and at any instant there is a finite concentration of RNH_3^+. The equilibrium constant for the above equilibrium is about 10^{-5}. In our system taking amine $10^{-3}\,M$, and $OH^- 10^{-2}\,M$ the RNH_3^+ turns out to be $10^{-6}\,M$ while Cu(III) is $10^{-5}\,M$. Contrary to the earlier discussion on the reactive form of *DTC* a decrease in rate with increasing $[OH^-]$ was observed in the present case. This could be due to the hydrolysed species of amine, the ammonium ion RNH_3^+ being the active species. Such presumptions are not uncommon in literature. For example, *Bell* and *Ramsden*[10] postulated the free amine as the reactive species in the bromination of alkyl amines even at as high H_2SO_4 concentration as $8\,M$. The observed salt effect points to a rate determining step between oppositely charged ions which also lends support to this view because monotelluratocuprate(III) bears a unit negative charge.

No kinetic or spectral evidence could be obtained to confirm the adduct formation proposed in the mechanism. The Cu-amine complexes in the mono and bivalent states of copper are quite common and the proposed adduct formation between copper in its trivalent state and amine receives support from the pulse radiolytic studies of *Mayerstein*[11] who generated Cu(III)-amine complexes which were found to have only transient existence. In the oxidation of amines both α-hydrogen atom transfer and electron transfer from the lone pair on nitrogen can occur depending on the structure of amine, oxidant, medium etc. The mechanism can be understood by viewing the reaction in two directions: (i) the ease of formation of free radicals, (ii) the ease of formation of the adduct. The authors propose an α-CH bond fission on the following grounds:

a) Benzyl amine studied by *Wie* and *Stewart*[12] is one of the most likely amines that react by α-hydrogen transfer not only because it is a primary amine but also the free radical produced in the hydrogen transfer process is resonance stabilized by benzene ring. Energy considerations show that 24 K cal/mol less energy is needed to form a benzyl free radical from toluene than to form a methyl free radical from methane[13] indicating that the benzyl radical is formed faster than the methyl radical. Our study revealed that benzyl amine reacts twice as fast as methyl amine which is fastest among the various other primary aliphatic amines.

b) Isotopic kinetic studies by *Rosenblatt* et al.[14] revealed that electron abstraction is predominant in tertiary amines. However in the present work it was found that the tertiary amines react much slower than primary and secondary amines.

c) The low reactivity of tertiary amines can also be ascribed to the difficulty in the formation of the adduct due to decrease in positive charge on the nitrogen caused by a + I effect and also steric effects. For the same reasons the ligand strengths of amines towards Cu(II) is given by: $NH_3 > RNH_2 > R_2NH > R_3N$ (Ref.[15]). The order of reactivity of amines was found to be secondary > primary > tertiary. The surprisingly high reactivity of the secondary amines may be ascribed to the former factor i. e., the ease of formation of alkyl free radicals which is in the order:

$$\dot{C}H_3 < CH_3\dot{C}H_2 < CH_3CH_2\dot{C}H_2 < (CH_3)_2\dot{C}H.$$

The order of reactivity of primary amines is: benzyl > methyl > ethyl $\simeq$ *n*-propyl $\simeq$ *n*-butyl $\simeq$ n-hexyl $\simeq$ isobutyl > cyclohexyl > isopropyl $\simeq$ *sec*-butyl amine (Table 1). The reverse trend in the

Table 1. *Activation parameters for DTC-amine reactions*

Amine	k'' at 300.5 K	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
	M^{-1} min^{-1}		kJ mol^{-1}		J mol^{-1} deg^{-1}
methyl	120	119	116	71.9	148
ethyl	46.1	119	116	74.3	140
n-propyl	35.7	123	120	75.0	150
n-butyl	41.5	107	105	74.6	100
n-hexyl	32.2	107	105	75.2	99.0
benzyl	184	105	103	70.9	106
cyclohexyl	22.3	99.6	97.1	76.1	70.0
isopropyl	9.46	99.6	97.1	78.3	63.0
sec-butyl	9.21	109	107	78.3	95.0
isobutyl	30.2	91.9	89.40	75.4	47.0
di *n*-butyl	473	99.6	97.10	68.5	95.0
di isopropyl	6.91	91.9	89.40	79.1	64.0
diethyl	990	109	107	63.7	143
trimethyl	15.9	99.6	97.1	77.0	67.0
triethyl	6.13	99.6	97.1	79.4	59.0

reactivities of the corresponding primary amines could only be explained by taking into account the ease of formation of the stable adduct.

The operation of various structural factors influencing reactivity has long been recognized from various kinetic studies, e.g., steric hindrance and substituent polarity. A method for separating polar and steric effects in ester hydrolysis was suggested by *Ingold* in 1930 and later developed by *Taft*[16,17]. According to *Taft* the linear free energy equation connecting the rate constants and polar as well as steric substituent constants is

$$\log k/k_0 = \rho^* \sigma^* + \delta E_s$$

where k and k_0 are rate constants of substituted and parent compounds, σ^* the polar substituent constants which are given for different groups on a relative scale, ρ^* the polar reaction constant, E_s the steric substituent constant and δ steric reaction constant.

The rates of oxidation of primary amines by Cu(III) were found to obey the *Taft* linear free energy relationship (Fig. 2). The reaction constant ρ^* was found to be 6.3 and this high value can be understood from *Taft*'s suggestion made above that polar effects of substituents are markedly higher for reactions in basic medium. The positive value of ρ^* indicates an electron deficient active centre as proposed in the mechanism. The δ value was found to be negligible for primary amines suggesting insignificant steric effects. The thermodynamic parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were evaluated and listed in Table 1.

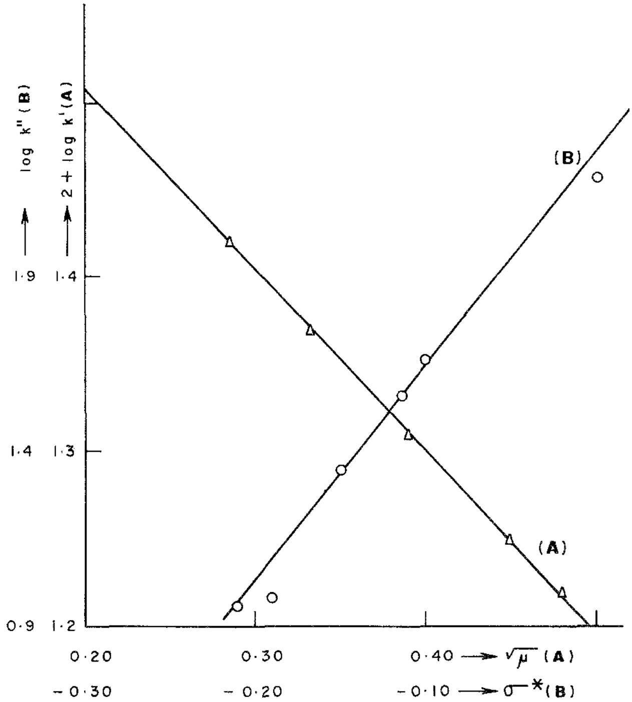

Fig. 2. *A* Effect of added salts on rate of reaction; *B* Effect of substituent: *Taft* plot of *DTC*-amine reaction

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