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KINETICS OF THE DIRHODIUM TETRAACETATE CATALYZED DECOMPOSITION OF ETHYL DIAZOACETATE IN 1,4-DIOXANE. IS NITROGEN INVOLVED IN THE TRANSITION STATE?

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Abstract

The rate of decomposition of ethyl diazoacetate (EDA) in 1,4-dioxane under bis-(hexafluoroacetoacetonato)copper(II) (HFAC) and of dirhodium tetraacetate (DRTA) has been measured in the temperature range 332-352ºK. While the copper catalyst promoted irregular and irreproducible decomposition of EDA in formal kinetic terms, DRTA promoted a smooth reaction that was first order in EDA. Apparent rate constants were in the range 3.0 - 12 x 10(-4)s(-1) within the indicated temperatures. The only product detected was the C-H insertion adduct of the putative EDA-derived rhodium carbene into a methylene group of dioxane. Activation parameters for the first order EDA transfiguration under DRTA catalysis were: $\Delta H^{\ddagger}$ = 16.4 ± 1.4 Kcal mol(-1), and $\Delta S^{\ddagger}$ = -25 ± 4 eu. The highly negative entropy of activation was deemed compatible with the coupling of EDA and DRTA without the exclusion of nitrogen during the rate determining step en route to the metal carbene.

INTRODUCTION

Diazoalkanes and alpha-diazocarbonyl compounds react with alkenes, alkynes, and hydrocarbons under the auspices of heat, UV-light, and some transition metal compounds.[1] There is general agreement that the former two proceed chiefly by decomposition of the diazo moiety into a free carbene that undergoes C-H insertion, cyclopropanation, and carbene dimerization.[2] Also, the formation of five-membered pyrazolines occurs by way of a 1,3-dipolar cycloaddition of the diazo nitrogen atoms onto the olefin. Then, the heterocycle may undergo thermal transfiguration to a cyclopropane.[1,2]

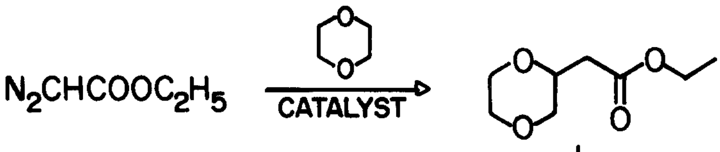
Catalytic methods have expanded considerably the thermal and photochemical schemes,[3] providing methods of preparative value for diazocompounds interactions with alkenes and alkynes, including C-H insertion,[1b] cyclopropanation,[1] addition-elimination,[4] and the production of oxacyclopentenes[5] and ylides.[6] In spite of its synthetic usefulness, the catalytic scheme is mechanistically complex to the point that several ways of interaction between the diazocompound, the catalyst, and the olefinic substrate are conceivable. The prevailing idea is that a metal carbene appears at some stage[7] as the consequence of a still undefined interaction between the metal atom and the diazo group that must be followed by the exclusion of a molecule of nitrogen. The transient electrophilic complex thus formed then transfers the bound carbene to some electronically dense organic substrate, thus liberating the metal catalyst and enabling it to start a new catalytic cycle.[8]

The majority of $L_nM{=}CR_2$ systems are unstable, specially when M= Cu, Rh, Pd, Ag. This, added to the various possible evolution pathways open to them have limited the number of studies devoted to the quantitative kinetic analysis of diazocompound/catalyst/substrate combinations. Most of the available data corresponds to relative rate studies of pairs of substrates,[7c,9] product analysis,[4e] and regioselectivity of metal carbenes with selected dienes.[7c,d,10] However, these methods lead only to relative activation parameters that belong to the reaction between metal carbene and substrate but provide little or no information as to the interaction of the diazocompound with the metal catalyst.

The high reactivity expected for the highly electrophilic $L_nM=CR_2$ complex makes it likely that the actual rate determining step (RDS) of the entire process belongs to the metal carbene forming step.[11b] Therefore, any rate study that measures directly the disappearance of the diazocompound should provide useful data of the mechanism involved in its interaction with the catalyst. The present study is aimed at developing such data, in particular for the C-H insertion reaction.

RESULTS AND DISCUSSION

Copper chelates[11] and rhodium carboxylates[12] are among the most widely used catalysts for diazocarbonyl decomposition. Similarly, ethyl diazoacetate (EDA) is by far the best well studied member of the extended family of diazocarbonyl derivatives.[13] Therefore, the bis(hexafluoroacetoacetonato)copper (II) (HFAC)[14] and dirhodium tetraacetate (DRTA)[12a] promoted decomposition of EDA in 1,4-dioxane was chosen as working model for kinetic studies. Both catalysts share the lack of affinity for weak Lewis bases.[15,16] In the absence of pi-substrates, it was assumed that the EDA derived metal carbene would undergo chiefly C-H insertion into any of the eight equivalent methylenic protons of dioxane



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The reaction of EDA with excess dioxane which was used as solvent, under synthetic conditions (see experimental section) using DRTA catalysis furnished adduct 1 (46% yield) along with ethoxycarbonylcarbene dimers diethyl fumarate and maleate (30%) and reduction adduct diethyl succinate (14%). Compound 1 was characterized by its proton NMR signals at δ 2.37 (part AB of an ABX multiplet, J_1= 6.0 Hz, J_2= 15.5 Hz) of the methylene alpha to the methylene group, in addition to the standard signals expected for this structure. The mass spectral data was also consistent with structure 1 (see experimental part). Under the conditions used for the kinetic measurements, characterized by high dilution of components (10^{-4}M) and excess dioxane solvent,[17] only adduct 1 was detected (GLC). Products derived from C-O insertion were not observed

Kinetics of the EDA conversion under HFAC catalysis:

HFAC is soluble in dioxane and its UV spectrum does not show an appreciable absorbance at the wavelength at which (248 nm) the decomposition of EDA was followed. Rather it displays maxima at 212 and 307 nm. HFAC promotes appreciable transformation of EDA at temperatures above 78ºC only. An equimolar solution (10^{-4} M) of EDA and HFAC in dioxane at 352 ± 0.2ºK featured a log|EDA| versus time plot in which three sectors of the resulting curve became apparent (Fig. I). During the first ten minutes little decomposition occurs. This period may correspond to the commonly observed induction time where reduction of copper(II) to copper(I) by the diazocompound takes place.[18] This period is followed by an abrupt decrease in EDA concentration. Visibly, a very active catalytic species of unknown nature is formed at this point which is rapidly exhausted since the concentration of EDA then falls to a nearly constant value. A lower HFAC/EDA molar ratio only lengthens the induction period. A similar behavior was observed when cyclohexene replaced dioxane as solvent. Further studies with the copper catalyst were thus discontinued, since in addition results were not reproducible.

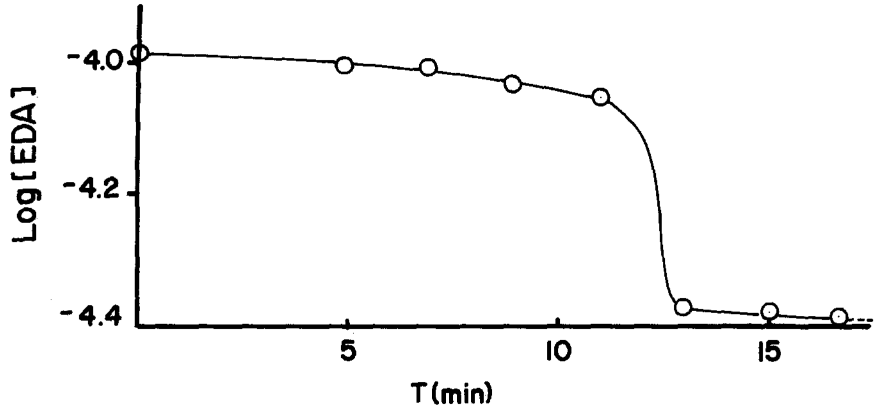


FIGURE I; Plot of log|EDA| vs time for a typical decomposition of EDA in cyclohexene under HFAC catalysis.

Kinetics of EDA conversion with DRTA catalysis:

This catalyst, first introduced by Teyssie and coworkers[12a] for the active decomposition of diazocarbonyl compounds, possesses only one vacant metal coordination site per metal atom. It exists in solution as a dimer, so in principle it may bind to as much as two molecules of EDA. It does not form complexes with olefins and weak Lewis bases.[16] Consequently, the interaction of EDA and DRTA in dioxane may be envisioned as a binary combination only. Any result stemming from kinetic data based on the disappearance of EDA basically should reflect this binary interaction.

As opposed to HFAC, the decomposition of EDA promoted by DRTA showed a good linear correlation in plots of log|EDA| vs time (r= 0.9950) at temperatures above 331ºK. At lower temperatures the process became too slow to be practically measurable. The first order constants for EDA fall in the order of 3 x $10^{-4}s^{-1}$. Predictably K_{obs} was found to be substantially modified by the DRTA/EDA relative ratio. These results are portrayed in Table I and Fig. II. Two sectors of this graph appear outstanding. At DRTA/EDA ratios below 0.3 the plot shows a slope of 6.94. The lower than expected rates of the first two points are likely to be due to the high dilution employed under which the rate is chiefly diffusion controlled. From this point onwards the slope decreases to a constant value of 1.51. A slope value of 1.0 should be attributed to the occupation of only one active site of the catalyst per mole of EDA,as it is presently accepted, whereas a slope equal to 2.0 should be interpreted as the coordination of the two rhodium atoms of DRTA with as many molecules of EDA. The intermediate value recorded here may result on the one hand from the partial dissociation of the rhodium dimer during its coordination with the first mole of EDA.[19] The liberated metal monomer then would still be able to bind and decompose EDA but at a slower rate.

TABLE I

Variation of the first order rate constants K_{obs} of EDA with modification of the DRTA/EDA relative concentration, using dioxane as solvent, at 332±0.2ºK. |EDA|= 1.0x10(-4) M.

|DRTA|/|EDA|	K_{obs} x 10^4 s^{-1}	r
0.1	0.7 ± 0.3	0.9231
0.2	1.6 ± 0.4	0.9755
0.33	2.1 ± 0.4	0.9764
0.5	2.3 ± 0.3	0.9833
0.67	2.5 ± 0.2	0.9912
1.0	3.1 ± 0.2	0.9950

Alternatively, the first coupling of EDA and DRTA may be followed by a second, less competitive coupling with a second mole of EDA on the other rhodium atom of the dimer that would retard sensibly the rate determining step. Both steps would lead to effective destruction of the diazo unit.

The likelyhood of catalyst dissociation raised the possibility that the liberated rhodium diacetate could bind competitively to an alkene molecule, were it be present in the reaction medium. This predicament is precluded for DRTA.[15] This being the case, the putative monomer would then be unable to contribute further to EDA decomposition and, as a consequence, K_{obs} should decrease. This hypothesis was tested by the introduction of potentially competitive alkenes of various electron densities and coordination capacity. The kinetics of the DRTA/EDA/dioxane system was reexamined using various concentrations of beta pinene, cyclohexene, and n-butylvinyl ether, as examples of non-coordinating and high electron density alkenes, respectively. However, K_{obs} remained unaltered within experimental error (K_{obs}= 3.1 ± 0.2 x 10^{-4} s^{-1}, r= 0.9899 for beta-pinene; K_{obs}= 3.0 ± o.2 x $10^{-4}s^{-1}$, r= 0.9928 for n-butylvinyl ether, at 333.0 ± 0.2ºK, all measurements up to 26% EDA conversion). A recent report on the relative reactivity of multiple pairs of olefins in EDA cyclopropanations catalyzed by DRTA[7c] showed a 3.5:1 relative reactivity ratio between n-butylvinyl ether and cyclohexene. The discrepancy with the EDA decomposition rates here reported may be explained on two accounts: 1) No cyclopropanation occurs in our case since our process is governed by the C-H insertion reaction. 2) The attack of alkenes on the strongly electrophilic DRTA/EDA derived carbene may be taking place, in all probability, after the RDS. The olefin discrimination[20] power recorded[7c] could be the consequence of the relative innate nucleophilic character of the pi system.

By contrast, a -20% change in K_{obs} was observed when a ten-fold increase in cyclohexene/EDA relative ratio (Table II) was used. This effect may be interpreted as a partial inhibition of the active site of the rhodium catalyst in monomeric form, that interferes negatively with the main course of the DRTA/EDA interaction, including the regeneration of the DRTA dimer that conceivably completes the catalytic cycle. The absence of cyclopropanation products (GLC evidence) even at the highest cyclohexene/EDA ratio (3:1) in dioxane suggested that the contraction of K_{obs} values was not due to an alternative outcome of the metal carbene. The obvious control experiment of measuring K_{obs} for the DRTA/EDA/cyclohexene system was deemed meaningless since it would involve not only a stark polarity change of the reaction medium but in addition the mechanism would turn to the production of ethoxycarbonyl norcarane which is a drastically different process. Nevertheless, our results are in agreement with Salomon's and Kochi's observation that olefins do retard the rate of diazocompound destruction under catalysis by some copper compounds.[11b]

TABLE II

Decomposition of EDA in dioxane induced by DRTA. Effect of cyclohexene/EDA relative ratio on EDA first order rate constants of decomposition at T= 333.0 ± 0.2ºK. |DRTA|/|EDA|= 1.0

|cyclohexene|/|EDA|	K_{obs} x 10^4 s^{-1}	r
0.2	3.5 ± 0.2	0.9970
0.5	3.3 ± 0.2	0.9952
0.8	3.3 ± 0.3	0.9910
1.6	3.1 ± 0.2	0.9955
2.0	3.0 ± 0.2	0.9975
2.5	2.9 ± 0.2	0.9869
3.0	2.9 ± 0.1	0.9969

The activation parameters for the DRTA/EDA/dioxane system were obtained using an Arrhenius plot in the temperature range 337-352ºK (Table III). At higher temperatures, the log|EDA| vs time graphs showed a deviation from linearity above 20% EDA conversion. This result could indicate a change in mechanism and thus the data was discarded. From the first order graphs (Fig III) the Arrhenius parameters were calculated (Table IV, entry 1)

As Table IV shows, the activation parameters for the EDA decomposition are rather sensitive to the particular reaction conditions, substrates used, and products formed. The highly negative entropy of

TABLE III

Decomposition of EDA in dioxane induced by DRTA. Effect of temperature on EDA first order rate constants. |DRTA|/|EDA|= 1

Entry	T (ºK)	K_{obs} x 10^4 s^{-1}	r
1	337.2 ± 0.2	4.5 ± 0.3	0.9978
2	343.1 ± 0.2	6.2 ± 0.3	0.9967
3	348.8 ± 0.2	9.5 ± 0.7	0.9977
4	352.0 ± 0.2	12.0 ± 1.2	0.9911

activation associated with the C-H insertion process (entry 1) falls roughly between the values reported for cyclopropanation (entries 2 and 3) and for 1,3-dipolar cycloaddition (entries 5 - 7). Our results are compatible with a highly ordered transition state in which dioxane is probably not involved since DRTA shows no affinity for this compound. This in turn suggests that nitrogen is not excluded during the RDS since its extrusion would be expected to increase considerably the entropy change. The formation of a diazocompound-metal complex in the RDS such as those reported for nickel, iron, titanium and vanadium[22] is conceivable.

TABLE IV

Selected activation parameters for the decomposition of EDA by some metal catalysts

Entry	Reaction system	main product	$\Delta H^{\ddagger}$ (Kcal mol^{-1})	$\Delta S^{\ddagger}$ (eu)	reference
1	EDA/DRTA/Dioxane	C-H insertion	16.4 ± 1.4	-25 ± 4	this work
2	EDA/DRTA/styrene	cyclopropanation	15.0 ± 0.6	-3.1 ± 2	15a
3	EDA/CuTf/1-hexene	cyclopropanation	19.1	-8.9	11b
4	EDA/PdOAc$_2$	carbene dimerization	NA	-30.0	15a
5	EDA/H$_2$C=CHCOOEt/Bz	1,3-dipolar addition	11.5	-39.2	21
6	EDA/H$_2$C=CHCN/Bz	1,3-dipolar addition	11.5	-49.9	21
7	EDA/H$_2$C=CHCN/Mo$_2$(OAc)$_4$	1,3-dipolar addition	11.3	-47.2	21

NA= not available. Bz= benzene

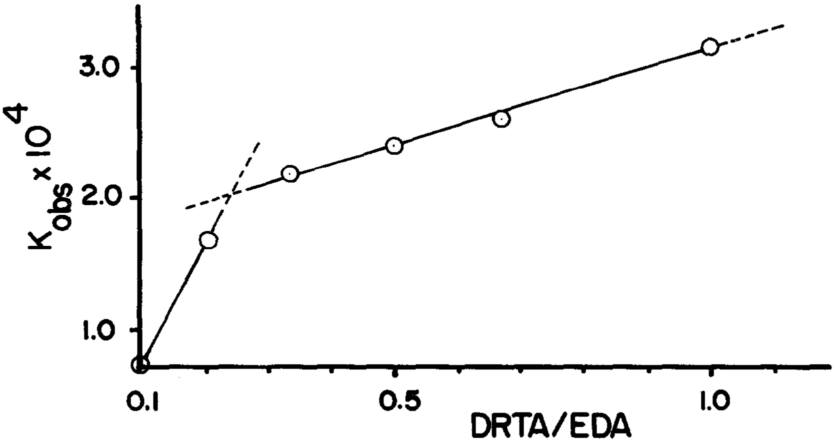


FIGURE II; Variation of first order rate constants of the decomposition of EDA catalyzed by DRTA in dioxane. Effect of DRTA/EDA relative ratio.

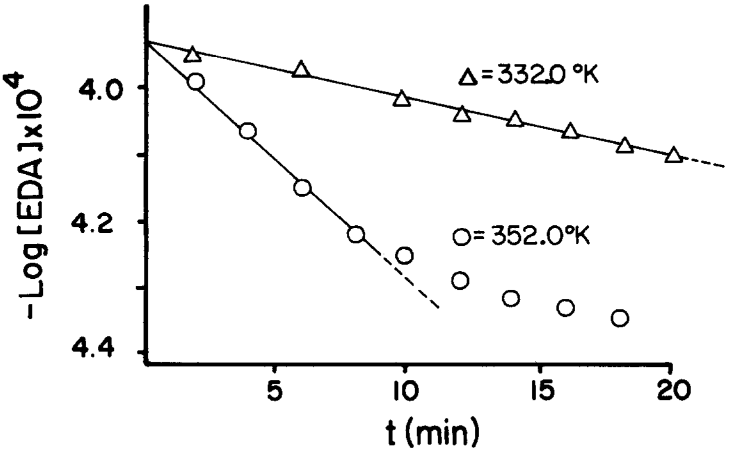
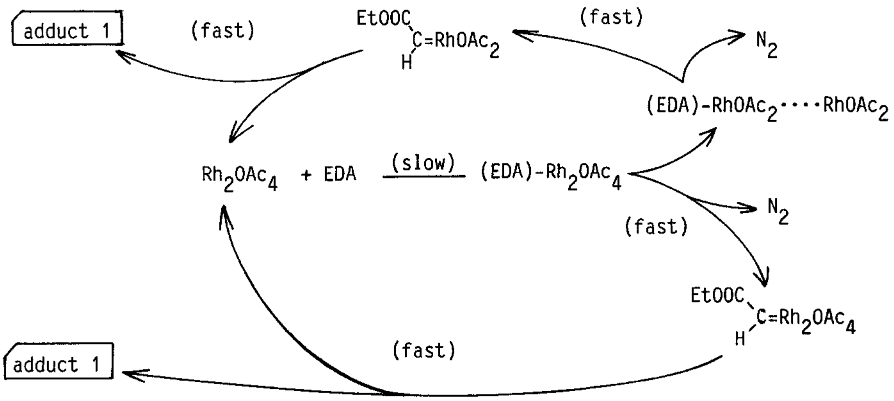


FIGURE III; Representative plots of -log |EDA| vs time. Effect of temperature in the range 332.0-352.0ºK. DRTA catalysis at DRTA/EDA = 1.0

One reaction sequence that is compatible with these facts appears portrayed in Scheme I. There, two divergent pathways stem from the initial construction of the DRTA-EDA couple, which according to present data would be the rate determining step. One route assumes that the rhodium dimer is never dissociated while the other includes partial or total splitting of the complex to form a monomeric metal carbene. The two alternative routes may be in mutual competition.

Although in principle the cyclopropanation reaction should follow a similar sequence of events, since the olefinic substrates required modify only marginally the rate constant of EDA decomposition, the much higher entropy of activation recorded for that reaction (entry 2) may be derived from the formation of a widely different transition state in which nitrogen is effectively excluded with the involvement of the alkene. Alternatively, this may be a very complex multistage process not accessible to classical kinetic studies.

SCHEME I



EXPERIMENTAL SECTION

Materials and Methods: Proton Magnetic Resonance spectra were recorded with a Varian Associates EM-390 spectrometer operating at 90 MHz and using tetramethylsilane as internal standard. Chemical shifts are reported downfield from TMS in delta units. Mass spectra were obtained from a DuPont 2149-B instrument operating in the EI mode at 70 eV. Gas chromatographic analyses were performed using a Hewlett-Packard 5710-A instrument fitted with a 12 ft 3% SE-30 on 80/100 supelcoport packed column using nitrogen as carrier gas and flame ionization detection. Liquid chromatographic analyses were run in a LDC double pump instrument using UV detection at 254 nm and a C-18 reverse phase column in water-methanol mixtures. UV spectra and quantitative determinations were recorded in a Pye Unicam model SP 1800 spectrometer in 1 cm quartz cells using dioxane as reference. HFAC^{14} and DRTA^{22} were prepared in the laboratory following published procedures and dried just prior to use under 90ºC and vacuum (10-20 torr) for three hours as standard conditions. Ethyl diazoacetate was distilled under vacuum before use.

Ethyl 2'-(1,4-dioxanyl)-acetate:

A three necked, round bottomed, one hundred mL flask fitted with addition funnel, reflux condenser, and a gas line was dried with a heat gun and filled with freshly distilled 1,4-dioxane (25 mL), and DRTA (50 mg) under a dry nitrogen atmosphere. Heat was applied (60ºC) and a solution of EDA (2.0 g) in dioxane (20 mL) was added dropwise over a two hour period. After the addition was complete the cold reaction mixture was filtered through a short pad of alumina act III. Evaporation of excess dioxane and vacuum distillation of the oily residue gave 2.9 g of colorless oil bp 65-75 (0.5 torr). The composition of this material was determined by GLC using dimethylphthalate as internal standard. It was composed of adduct 1 (46%), diethyl fumarate and maleate (30%), and diethyl succinate (14%). Thick layer chromatography on Silica gel 60 plates using pet ether (bp 40-70º)/chloroform 1:1 allowed the isolation of 1 as a colorless oil bp 70º (0.4 torr); ir (neat) 3020(s), 1730(s), 1475(s), 1395 (s), 1245(s), 1205(s), 1120(s), 1035(s), 1005(s), 970(s), 915(s); nmr ($CDCl_3$) δ 1.27 (t, 3H, J= 6.0 Hz CH_3-), 2.37 (dq, 2H, J_1= 6.0 Hz, J_2= 15.5 Hz, CH_2-C=O), 3.5-3.8 (m, 6H, 3xCH_2-O), 4.33 (q, 2H, J=6.0 Hz, CH_2-CH_3) ppm; mass spectrum e/m(%): 174 (M^+, 31%), 101 (M^+-COOEt, 89%), 87 (M^+-CH_2-COOEt, 100%) 60 (53%). Analysis: calculated for $C_8H_{14}O_4$: C, 55.14; H, 8.11; O, 36.76. Found: C, 55.02; H, 8.18; O, 36.80.

Kinetics of the Reactions of Ethyl Diazoacetate in Dioxane:

Stock solutions of EDA were prepared by dissolving 1.14 g of it in dioxane for a total 1L volume. 1 mL of this solution was then taken up to 100.0 mL by the addition of dioxane. Stock solutions of DRTA were prepared by dissolving 442 mg of this material in sufficient dioxane for a 1.0 L volume. Then 10 mL of this solution were diluted to 100 mL using dioxane. For all kinetic runs both solutions were preheated separately at the operating temperatures for 15 min. At time zero the catalyst and diazocompound solutions were rapidly mixed and magnetically stirred at constant temperature (±0.2ºC) under a nitrogen atmosphere free of oxygen and moisture. Aliquots were withdrawn at 2 min intervals through a rubber septum with the aid of a syringe and inmediately frozen. Control experiments showed that no appreciable decomposition of EDA occurred at room temperature after two hours owing to the high dilution employed. Each aliquot was divided into two 2 mL portions. One fraction was then subject to chromatographic quantitation of EDA contents using HPLC while the UV spectrum of the other was measured using the band at 248 nm as EDA concentration indicator. Results of both methods were found comparable within experimental error. Each kinetic run was performed in triplicate. Errors for rate constants, enthalpy and entropy of activation were calculated by least square linear regression analysis using a Lotus spreadsheet program fashioned by the authors on an Atari 520ST microcomputer, and using 95% confidence limits factor. For some representative experiments, aliquots were also monitored for production of adduct 1 by GLC using conditions indicated above. Values derivec from GLC data were comparable with that calculated on the basis of UV and HPLC data, within experimental error. GLC data of actual kinetic runs showed complete absence of ethoxycarbonyl dimerization products.

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