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MECHANISMS OF DECOMPOSITION OF DIETHYL DIAZOSUCCINATE

THE SOLVENT EFFECT ON THE EXTENT OF CARBENE AND CARBONIUM ION INTERMEDIATES

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Abstract—Both kinetic and product studies on the decomposition of diethyl diazosuccinate in various solvents are described. The decomposition in the aprotic solvents such as diglyme and mesitylene proceeds through the carbene intermediate, while that in hydrochloric acid through the carbonium ion. The reaction in the protic solvents such as ethanol and cyclohexanol involves mainly the carbene intermediate. The decomposition in acetic acid is a borderline case, involving both intermediates.

INTRODUCTION

The 1,2-hydrogen migration reaction of an aliphatic diazo compound via a divalent carbon leads to an olefin. Such rearrangement is of theoretical interest and also a synthetically useful reaction.[1,2] Considerable efforts have been made to clarify the real features of the 1,2-hydrogen migration, and present known facts are: (i) the spin state of the divalent carbon (single state),[3-6] (ii) the stereochemistry,[7-10] and (iii) the solvent effect.[11,12]

The decomposition mechanisms of diazo and related compounds in protic and aprotic solvents have been extensively studied. In principle, the reaction in protic solvents involves prior protonation, to give the carbonium ion after loss of nitrogen, while that in aprotic solvents proceeds through the carbene intermediate.[1,13,14] Such investigations are mainly concerned with the alkyl or aryl group migration to a divalent carbon (Bamford–Stevens reaction[1]), the carbonyl group migration (Wolff rearrangement[1]), and the addition reaction to olefins.[15]

However, the solvent effect on the 1,2-hydrogen migration reaction of diazo compounds has been little studied. Two of us previously reported, in preliminary form, that even in the protic solvents the carbene intermediate is involved for the migration reaction of diethyl diazosuccinate.[11] We now wish to report a full account of our research in this area.

RESULTS AND DISCUSSION

1. *Kinetic study.* The decomposition of diethyl diazosuccinate (**1**) was studied in diglyme, ethanol-HCl, ethanol, and glacial acetic acid over appropriate ranges of temperature. The decomposition of **1** in diglyme in the temperature range 110–145° obeys first-order kinetics. The first-order rate constants in Table 1 were obtained from the usual first-order plot.

Least-squares treatment of the results yields

$$k = 10^{11\cdot 77 \pm 0\cdot 26} \exp(-27\cdot 31 \pm 0\cdot 47/RT)\ \mathrm{sec}^{-1}$$

in which $R = 0\cdot 00198$ kcal mole^{-1} deg^{-1}; the standard deviation is cited in each case. The value of the A factor appears to suggest that the decomposition of the diazoester **1** in the aprotic solvent is unimolecular. The first-order rate constants in diglyme will be denoted k_c (carbenic) henceforth.

The decomposition of **1** in ethanol-aq. HCl solvent occurs at lower temperature (20–50°) and it will be shown that the reaction is acid-catalyzed. The results are given in Table 2. Least-squares treatment in these data yields the following Arrhenius equation:

$$k_{app}(\mathrm{ethanol} - 0\cdot 025\ \mathrm{M\ HCl}) = 10^{8\cdot 61 \pm 0\cdot 20} \exp(-16\cdot 58 \pm 0\cdot 28/RT)\ \mathrm{sec}^{-1}$$

Many acid-catalyzed reactions show mixed-order kinetics in which the rate can be expressed as the sum of two terms, for example

$$\mathrm{Rate} = k_c[\mathrm{diazoester}] + k_d[H_3O^+][\mathrm{diazoester}]$$

where in this particular case

k_c = first-order rate constant for carbenic process

k_d = second-order rate constant for diazonium process.

If the above equation is divided through by [diazoester], an expression for the apparent first-order rate constant, rate/[diazoester], is given by

$$k_{apparent} = \mathrm{Rate}/[\mathrm{diazoester}] = k_c + k_d[H_3O^+].$$

The apparent first-order rate constants were plotted against $[H_3O^+]$ in Fig. 1. From the slope of the straight line it is found that the value for k_d (ethanol-0·025 M HCl) at 40·5°C is $4\cdot 5 \times 10^{-2}$ lit mole^{-1} sec^{-1}. It is also apparent from such a plot that the reaction is first-order in the protonated species since $k_{apparent}/[H_3O^+]$ yields a constant value. The most striking feature of this plot is the intercept of the straight line which corresponds to a very small value for k_c. The acid-catalyzed decomposition of 3-diazobutan-2-one shows similar behavior.[16] It is clear that

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*To whom correspondence should be addressed. Joint publication was decided on after we learned of our related research in this area.

Table 1. First-order rate constants for the decomposition of diethyl diazosuccinate (0·22 M) in diglyme

Temp(°C)	110.5	120.5	125.5	130.5	135.5	145.5
10^4k(sec^{-1})	1.57 ±0.03	4.15 ±0.05	6.28 ±0.05	9.45 ±0.10	13.70 ±0.10	32.90 ±0.20

Table 2. Apparent rate constants for the decomposition of diethyl diazosuccinate (0·22 M) in ethánol-aq. HCl

Temp(°C)	Concentration	10^4k_{app}(sec^{-1})
20.5	ethanol-0.025 M HCl/6.94 M H_2O	1.92 ± 0.02
30.5	ethanol-0.025 M HCl/6.94 M H_2O	4.71 ± 0.05
40.5	ethanol-0.0125 M HCl/6.94 M H_2O	5.76 ± 0.06
40.5	ethanol-0.025 M HCl/6.94 M H_2O	11.20 ± 0.12
40.5	ethanol-0.0375 M HCl/6.94 M H_2O	17.60 ± 0.10
50.5	ethanol-0.025 M HCl/6.94 M H_2O	26.87 ± 0.22

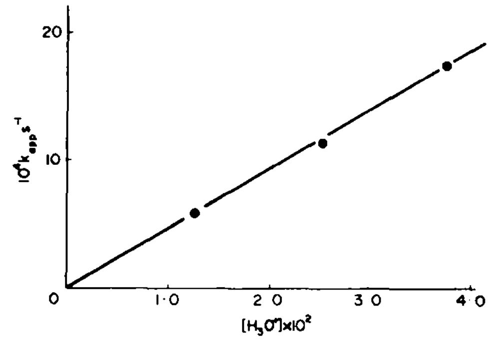


Fig. 1. Plot of first-order rate vs $[H_3O^+]$

the decomposition of **1** in ethanol-0·025 M HCl solvent is almost exclusively by the protonation of the diazoester since $k_d > k_c$. The value of k_c at 40·5° calculated from the Arrhenius parameters in diglyme is of the order 10^{-7} sec^{-1}.

Further confirmation of catalytic decomposition of **1** in ethanol-HCl solvent was obtained from the studies on the effect of water on the rate of decomposition. The results are given in Table 3. It is seen that the reaction rate is decreased by the presence of trace amounts of water. Similar effects have been observed in many acid-catalyzed reactions.[17] It is generally agreed that an equilibrium of the following kind is established:

$$C_2H_5OH_2^+ + H_2O \rightleftharpoons C_2H_5OH + H_3O^+.$$

Since water is more basic then ethanol, the equilibrium will favor the formation of hydronium ion. The inhibitive effect of water on acid-catalyst reaction can be explained. The ethyloxonium ion $C_2H_5OH_2^+$ is thought to be more effective protonation species than the corresponding hydronium ion.

The decomposition of **1** was also carried out in anhydrous ethanol at 40·5° and the observed first-order rate constant was of the same order of magnitude, *ca*, 10^{-7} sec^{-1}, as that in diglyme. It can be concluded that the decomposition of **1** in anhydrous ethanol is similar to that of the decomposition in aprotic solvents i.e. a carbenic process. It is unfortunate that a temperature study could not be made because of the volatility of the solvent.

Finally, the decomposition of **1** was carried out in glacial acetic acid. The results were tabulated in Table 4. It is noted that the temperature range for the decomposition is similar to that in ethanol-aq. HCl solvent. The

Table 3. Apparent rate constants at 40·5°C for the decomposition of diethyl diazosuccinate (0·22 M) in anhydrous and aqueous ethanol-HCl mixture

Condition	10^4 k_{app}(sec^{-1})
Anhydrous ethanol - 0.0125 M HCl	12.79 ± 0.12
Ethanol/0.0125 M HCl/1.67 M H_2O	9.87 ± 0.10
Ethanol/0.0125 M HCl/3.33 M H_2O	7.78 ± 0.08
Ethanol/0.0125 M HCl/6.94 M H_2O	5.76 ± 0.06

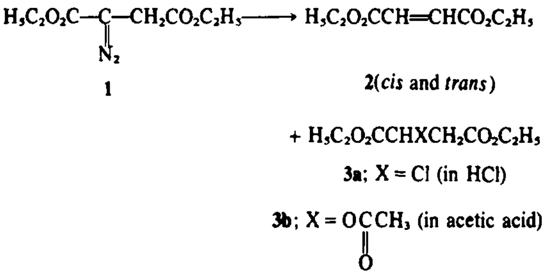
Table 4. Apparent rate constants for the decomposition of diethyl diazosuccinate (0·23 M) in glacial acetic acid

Temp (°C)	30.5	40.5	50.5	60.5
10^4 k (sec^{-1})	5.17±0.03	11.20±0.08	25.33±0.22	52.64±0.50

Arrhenius equation for the apparent rate constant is given as follows:

$$k_{\text{apparent}}\,(\text{acetic acid}) = 10^{8.00\pm0.16}\exp(-17{\cdot}70 \pm 0{\cdot}23/RT)\ \text{sec}^{-1}.$$

2. *Product study*. The decomposition of **1** in various solvents gives the olefin (**2**) in the range of *ca*. 30–90 per cent yield, and the corresponding substitution products in the case of acetic and hydrochloric acids (Eqn 1). The results are summarized in Table 5.



$$\underset{\textbf{1}}{H_5C_2O_2C\!-\!\underset{\underset{N_2}{\|}}{C}\!-\!CH_2CO_2C_2H_5} \longrightarrow \underset{\textbf{2}(\textit{cis}\text{ and }\textit{trans})}{H_5C_2O_2CCH{=}CHCO_2C_2H_5}$$

$$+\ H_5C_2O_2CCHXCH_2CO_2C_2H_5$$

3a; X = Cl (in HCl)

3b; $X = O\underset{\underset{O}{\|}}{C}CH_3$ (in acetic acid)

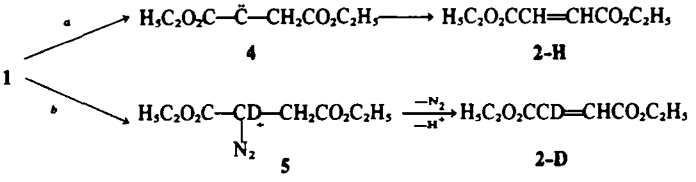
There may be two possible pathways for the olefin formation reaction, namely, the 1,2-hydrogen migration onto the carbene (*path a*) and the beta-elimination of H^+ via the diazonium (or carbonium) ion (*path b*). When the decomposition is carried out in a deuterated solvent, the two paths can easily be distinguished by the analysis of the reaction products. If the olefin results from *path a*, an external deuterium is not incorporated into the olefin, because the process involves merely the intramolecular 1,2-hydrogen migration to the divalent carbon. On the other hand, *path b* involves a prior addition of D^+ from

Table 5. Decomposition products of diethyl diazosuccinate in the various solvents

Solvent	1,2-Hydrogen migration product, **2** (%)	Substitution product, **3** (%)
HCl	33	66 (**3a**)
CH_3CO_2H	32	64 (**3b**)
C_2H_5OH	80	–[a]
$C_6H_{11}OH$	82	–[a]
Diglyme	86	–
Mesitylene	93	–

[a] Small amounts of unidentified products were detected with vpc, presumably the corresponding alkoxy substituted products.

the solvent to 1, leading to alpha-deuteriodiazonium ion (5). The beta-elemination of the diazonium ion should give the olefin (2-D) where 50 per cent of the olefinic protons is deuterated if the elimination is so rapid that further replacement of the hydrogen by deuterium does not occur in the carbonium ion intermediate (Eqn 2).



The decomposition of 1 was carried out in several deuterated solvents. The resultant olefin was isolated and purified using a preparative VPC. The percentage of the deuterium incorporated into the olefinic position was determined from the analysis of the NMR spectra. Controlled experiments indicated that the olefinic hydrogen of 2 was not replaced by a deuterium in the solvent during the reaction and isolation procedures. The results are summarized in Table 6.

As is apparent from Table 6, the decomposition of 1 in the mineral acid proceeds through the diazonium and/or carbonium ion process *b*. The deuterium incorporation of 51 ± 3 per cent indicates that the further replacement of hydrogen by deuterium at the carbonium ion stage does not take place in hydrochloric acid. Consequently, the generally accepted concept, the carbonium ion process in a protic medium, holds good for the 1,2-hydrogen migration reaction of 1 in hydrochloric acid.

On the other hand, in acetic acid-d_1, the incorporation of deuterium was found to be 17 per cent, indicating that only 34 per cent of the olefin was produced via the *path b*. The major process (66%) was carbenic migration *a*.

The olefin resulted from the decomposition in the deuterated alcoholic solvent such as ethanol or cyclohexanol was incorporated 11 per cent or 4 per cent of deuterium respectively. Most of the olefin was produced through 1,2-hydrogen migration via the carbene intermediate (4).

Table 6. Deuterium incorporation into the olefin obtained in thermal decomposition of diethyl diazosuccinate

Solvent	D incorporated into 2 (%)	Carbenic process a (%)
$DCl-D_2O$[a]	51 ± 3	0
Acetic acid-d_1[a]	17 ± 3	66
Ethanol-d_1	11 ± 5	78
Cyclohexanol-d_1	4 ± 2	92

[a] The corresponding substitution product (3) were deuterated in the alpha-position; $H_5C_2O_2CCDCH_2CO_2C_2H_5$

3. CONCLUSION

The decomposition in diglyme is a unimolecular reaction with the energy of activation of *ca.* 27 kcal. This is of the right order of magnitude for the carbene reactions. For example, that for the thermal decomposition of diazomethane is 32 kcal[18] and that for the thermal decomposition of diazirines is in the range of 26–32 kcal.[19]

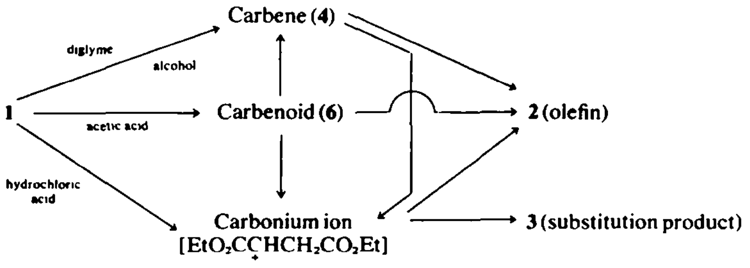
The reaction in hydrochloric acid is acid-catalyzed. The energy of activation is *ca.* 16 kcal, which is of the right order for a carbonium ion process of a diazo compound.[13c] The product study also supports this conclusion.

Consequently, the decomposition in diglyme and in hydrochloric acid is straightforward. The traditional concept, carbene in aprotic and carbonium ion in protic solvents, is doubtless valid for these two cases.

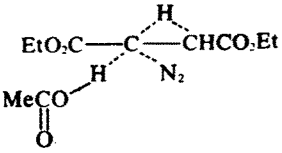
The kinetic study indicates that the carbene intermediate is involved at the transition state of the decomposition even in the alcohols. The product study shows that small amounts of deuterium are incorporated into the olefin. Consequently, the alcohols are not reacting prior to the decomposition, but presumably react with the carbene after the transition state. Similar results were obtained by the kinetic study on the decomposition of diaryldiazomethanes in alcohols, where the addition of alcohols has little effect on the rate of decomposition.[20]

In acetic acid, the product study reveals that olefin formation (32%) involves the carbene as the major path (66%), and that the substitution reaction (64%) involves the carbonium ion since the alpha - deuterio - alpha - acetoxy - succinate is formed in acetic acid-d_1. Accordingly, the carbene intermediate occupies 21 per cent of the whole reaction of 1. On the other hand, the energy of activation is *ca.* 16 kcal, similar to that in hydrochloric acid. This indicates that the decomposition involves the participation of acetic acid at the transition state before loss of nitrogen. If the free carbene such as that in diglyme were involved to some extent (21%) at the transition state, the activation energy should deviate from 16 kcal.

Consequently, we are forced to postulate the *carbenoid* intermediate (6) in this particular solvent. The olefin will be produced either directly via 6, or via the carbene and/or carbonium ion derived from 6. The complete protonation in 6 will lead to the substitution product (3) via the carbonium ion. A carbenoid species is postulated for the acid-catalyzed addition of phenyldiazomethane to olefins.[15]



Scheme 1.



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The pathways of the decomposition are summarized in Scheme 1.

EXPERIMENTAL

All temps were uncorrected. IR spectra were recorded with a Hitachi-S2 spectropotometer. NMR spectra were obtained by a Japan Electron Optics JNM-4H-100 spectrometer. Chemical shifts were given in τ-scale together with splitting patterns and relative integrated area. VPC analyses were carried out using a Yanagimoto 5DH with a 5·25 m × 0·3 cm column packed with Carbowax 20 M or Apiezon.

Diethyl diazosuccinate (**1**). This was prepared according to the method previously described.[8]

Solvents. Ethanol, cyclohexanol, diglyme, mesitylene, and glacial acetic acid were purified with a normal method. The deuterated solvents were commercially available from Nakarai Chemicals except cyclohexanol-d_1. This deuterated alcohol was prepared with a deuterium exchange reaction in large excess D_2O.

Kinetic procedure. The reaction was carried out by mixing a specific amount of **1** with appropriate thermo-equilibrated solvent in the reaction vessel, which was immersed in the oil bath and connected to a gas burette. The first-order rate coefficients were determined graphically from the plot of log $(V_\infty - V_t)$ against time where V_∞ was the volume of N_2 measured at infinite time and V_t was that at time t.

Decomposition of **1** *in various solvents.* A mixture of **1** (2·0 g) and 10 ml of a solvent was kept at an appropriate temp. After an essentially quantitative amount of N_2 was evolved, 20 ml water and 10 ml ether were added. The organic layer was separated, and further extraction with ether was carried out twice. The combined extract was dried over anhyd K_2CO_3. The yields of products were determined using an internal standard method with VPC. Besides, the products were isolated via distillation and purified with preparative VPC.

Diethyl Maleate and fumarate (**2**). These products were identified by comparison with the authentic samples which were commercially available.

1,2 *Dicarboethoxy*-1-*chloroethane* (**3a**). This was distilled from the reaction mixture; b.p. 85–87° (1 mm); IR (neat) 1745, 1290, 1200, 1035 cm^{-1}; NMR (in CCl_4) 5·48–5·63 (m, 1 H), 5·71–6·03 (m, 4 H), 6·82–7·38 (octet, 2 H), 8·64–8·85 (triplet–triplet, 6 H). (Found: C, 46·20; H, 6·22; Cl, 16·52. Calcd. for $C_8H_{13}O_4Cl$: C, 46·05; H, 6·28; Cl, 16·79%).

1,2 *Dicarboethoxy*-1-*acetoxyethane* (**3b**). This was distilled from the reaction mixture; b.p. 107–108° (2 mm); IR (neat) 1750, 1376, 1280, 1210, 1180, 1098, 1070, 1028 cm^{-1}; NMR (in CCl_4) 4·67–4·82 (t, 1 H), 5·73–6·00 (m, 4 H), 7·22–7·32 (d, 2 H), 7·94 (s, 3H), 8·64–8·84 (triplet–triplet, 6 H). (Found: C, 51·68; H, 7·03. Calcd. for $C_{10}H_{16}O_6$: C, 51·72; H, 6·94%).

Decomposition in deuterated solvents. DCl (20% DCl in D_2O, D_{min} 99%), CH_3CO_2D (99% D), C_2H_5OD (99% D), and $C_6H_{11}OD$ (85% D) were employed. The percentage of deuterium incorporation into the olefin was calculated from the integral area ratio of the olefinic proton (3·85 τ). The corresponding substitution products showed the following PMR spectra; **3a**-d_1 (in CCl_4) 5·71–6·03 (m, 4 H), 6·82–7·32 (qu, 2 H), 8·64–8·85 (tr–tr, 6 H); the absorption of the proton directly attached to the carbon connected with chlorine was completely disappeared; **3b**-d_1 (in CCl_4) 5·72–5·99 (qu–qu, 4 H), 7·27 (s, 2 H), 7·93 (s, 3H), 8·65–8·84 (tr–tr, 6 H); here also, the absorption of the proton directly attached to the carbon connected with acetoxy was completely disappeared.

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