gratefully acknowledge support for this work by the USAF, which sponsored one of us (T.A.M.). The financial support of the National Science Foundation is acknowledged with gratitude.

Registry No. **1a**, 5675-64-9; **1b**, 32363-36-3; **1c**, 63840-06-2; **1d**, 102697-49-4; **1e**, 102697-50-7; **1f**, 22827-60-7; **1g**, 102697-51-8; **1h**, 5434-63-9; **1i**, 86367-70-6; **1j**, 13294-86-5; **1k**, 3008-09-1; **1l**, 6004-64-4; **1m**, 7673-68-9; **1n**, 92855-58-8; **1o**, 6372-65-2; **1p**, 58286-92-3; **1q**, 102697-52-9; **1r**, 102697-54-1; **1s**, 1871-17-6; **1t**, 1521-59-1; **1u**, 102697-55-2; **1v**, 21438-92-6; **2a**, 86367-71-7; **2α**, 113160-97-7; **2b**, 113160-80-8; **2β**, 113160-96-6; **2c**, 113160-81-9; **2d**, 113160-82-0; **2g**, 113160-83-1; **2j**, 113160-86-4; **2l**, 113160-85-3; **2m**, 113160-84-2; **2n**, 113160-95-5; **2o**, 113160-93-3; **2q**, 113160-94-4; **2s**, 113160-87-5; **2t**, 113160-92-2; **2u**, 113160-89-7; **2v**, 113160-91-1; **2w**, 113160-90-0; **2x**, 113160-88-6; **2y**, 118514-16-2; **2z**, 113160-98-8; **6**, 118514-15-1; **7a**, 120-12-7; **7α**, 523-27-3; **7b**, 781-43-1; **7β**, 113705-11-6; **7c**, 1624-32-4; **7d**, 10210-26-1; **7g**, 56272-36-7; **7j**, 73016-10-1; **7l**, 67263-73-4; **7m**, 7044-91-9; **7n**, 33685-60-8; **7o**, 53760-37-5; **7q**, 118514-17-3; **7s**, 604-66-0; **7u**, 2395-97-3; **7v**, 28871-52-5; **7w**, 10075-86-2; **7x**, 10075-83-9; **7y**, 1545-69-3; **7z**, 605-48-1; **8**, 140-88-5; **9**, 814-68-6; **11a**, 65121-51-9; **11b**, 118514-18-4; **11c**, 84050-69-1; **11d**, 84050-70-4; **12a**, 113160-99-9; **12b**, 113161-00-5; **14**, 59045-59-9; **15**, 58791-50-7; **16**, 113180-35-1; **18**, 118514-19-5; **19**, 113161-01-6; **20**, 13979-56-1; **22**, 118514-20-8; **23**, 118514-21-9; **24**, 1089-56-1; **25**, 1624-34-6; **26**, 54974-11-7; **27**, 118514-22-0; **28**, 118514-23-1; **29**, 13719-98-7; **30**, 13387-48-9; **31**, 529-85-1; **32**, 107264-00-6; **33**, 107263-95-6; **34**, 107264-06-2; **35**, 62-53-3; **36**, 121-69-7; DDQ, 84-58-2; ethylene, 74-85-1; isopropylene, 563-45-1; *tert*-butylethylene, 558-37-2; (trimethylsilyl)ethylene, 754-05-2; 4-bromo-1-butene, 5162-44-7; 9,10-bis(chloromethyl)anthracene, 10387-13-0; 1,10-decanedithiol, 1191-67-9; veratrole, 91-16-7; acetaldehyde, 75-07-0; 9,10-dimethyl-2,3,6,7-tetramethoxyanthracene, 13985-15-4; acrylonitrile, 107-13-1; deuterium, 7782-39-0; maleimide, 541-59-3; *N*-methylmaleimide, 930-88-1; *N*-phenylmaleimide, 941-69-5.

Micellar-Induced Selectivity and Rate Enhancement in the Acid-Catalyzed Cyclization and Rearrangement of Monoterpenes. The Solvolysis of Linalyl and Geranyl Acetates

Benjamin C. Clark, Jr.,* Theresa S. Chamblee, and Guillermo A. Iacobucci

Corporate Research and Development Department, The Coca-Cola Company, P.O. Drawer 1734, Atlanta, Georgia 30301

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The monoterpene linalyl acetate (**1**) undergoes acid-catalyzed solvolysis/cyclization at pH 3 in HCl/citrate buffer to yield three major acyclic alcohols, geraniol (**2**), linalool (**3**), and nerol (**4**), and one cyclic alcohol, α-terpineol (**5**). The acyclic/cyclic alcohol ratio is 2.7 in no sodium dodecyl sulfate (SDS) controls after ca. 3 half-lives, compared to 8.5 when the reaction is carried out in a SDS micelle. No micellar rate effect was observed. The SDS-induced selectivity is explained in terms of the micelle-favoring acyclic conformers of linalyl acetate. In contrast to linalyl acetate, solvolysis of geranyl acetate (**6**) in the SDS micelle at pH 2 gives little product selectivity but yields a 7-fold rate effect relative to no SDS controls. This rate effect results in very different product distributions after 90% completion of the reaction. The observed SDS rate effect for geranyl acetate is compatible with a difference in solvolysis mechanism for linalyl and geranyl acetate.

Introduction

Despite the importance of functionalized mono- and polyene acid-catalyzed cyclizations,[1] rearrangements,[2] and ester solvolyses,[3] both to the synthesis and biogenesis of terpenes, reports of the effects of micelles on these reactions have been sparse. In fact, only a few reports of micellar effects on nonphotochemical cyclization reactions have appeared.[4-6]

We recently reported[4] a relatively large micellar-induced stereoselectivity and a modest rate enhancement in an acid-catalyzed "ene" cyclization of the monoterpene citronellal. Bunton and Cori[6] have also observed some micellar-induced selectivity in the cyclization/rearrangement of geranyl and neryl phosphates and pyrophosphates. In addition, sodium dodecyl sulfate (SDS) rate inhibition has been noted for some unusual neryl esters,[7] and the effect of compressed vs expanded films on nerol and geraniol solvolyses has been reported.[8]

We now report our observations showing that SDS micelles exert considerable product selectivity in the solvolysis of linalyl acetate with no rate acceleration, while a modest rate acceleration with very little selectivity was observed in the solvolysis of geranyl acetate. Even though hundreds of kinetic studies of organic substrates in micelles have been reported, very few involve complete quantitative product analysis over the course of the reaction as reported here. This type of detailed analysis is necessary to observe selectivity in complex reactions, and thus relatively few reports exist describing micellar selectivity. Studies limited to analysis of starting materials would have yielded very little information for the systems discussed here.

Due to their implication in terpene biogenesis, the acid-catalyzed solvolyses of geranyl, linalyl, and neryl systems employing many different esters and other substituents have been widely reported.[3] Specifically, the acetates have been investigated[9] in aqueous acid under conditions similar to those reported here. As noted by Juršič et al.,[7] water is the solvent of choice for studying

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Table I. Effect of SDS on Linalyl Acetate Solvolysis: Rate Data at 25 °C

kinetic parameters	HCl/citrate buffer reaction 1	HCl/citrate buffer reaction 2	HCl/citrate buffer/2% MeOH	SDS/HCl/citrate buffer
k_{obsd}, h^{-1}	8.70 (10^{-2})	1.05 (10^{-1})	9.60 (10^{-2})	1.05 (10^{-1})
$t_{1/2}$, h	7.97	6.59	7.22	6.58
pH	3.08	3.09	3.10	3.11
k_{abs}[a]	1.05 (10^{2})	1.29 (10^{2})	1.21 (10^{2})	1.24 (10^{2})
C_0 (calcd molar concn)	3.2 (10^{-4})	3.0 (10^{-4})	2.9 (10^{-4})	3.1 (10^{-4})
coeff of determ	0.999	0.999	0.999	0.999

[a] $k_{abs} = k_{obsd}$ (h^{-1})/[H^+] (mol/L) = L mol^{-1} h^{-1}.

Table II. Effect of SDS on Solvolysis of Linalyl Acetate at pH 3.1: Product Data at 25 h[a]

products[c]	concn of product, mole %[b] HCl/citrate buffer reaction 1	HCl/citrate buffer reaction 2	HCl/citrate buffer/2% MeOH	SDS/HCl/citrate buffer
linalool (3)	54.32	47.58	46.33	53.79
linalyl acetate (1)	10.50	7.15	9.04	7.14
α-terpineol (5)	23.69	21.05	19.39	8.69
neryl acetate (7)	2.38	2.33	2.25	0.90
geranyl acetate (6)	4.39	4.00	4.09	1.57
nerol (4)	2.87	2.68	2.60	4.21
geraniol (2)	8.15	7.25	7.20	15.94
total (% recovery)	106.30	92.04	90.90	92.24

[a] Approximately 3 half-lives. [b] Employing tetradecane as an internal standard and correcting for response; based on C_0 values in Table I. [c] In order of increasing retention time on Triton 305X.

bioorganic mechanisms, and aqueous micelles are the simplest models for biomimetic processes.

Results and Discussion

Solvolysis of Linalyl Acetate. Linalyl acetate (1) was allowed to react in 0.05 M HCl/citrate buffer, pH 3.1, with and without SDS, at a concentration of 0.3 mM, just below its solubility limit. An SDS concentration of 38 mM, well above its critical micelle concentration (cmc) of 8 mM, was employed resulting in a very low loading of substrate per micelle. In addition, the reaction was run in 2% MeOH/buffer, which yielded rate and product results the same as pure buffer but gave instantaneous solution of linalyl acetate compared to ≈3 h required in buffer only.

Comparison of the rate of linalyl acetate reaction for SDS/buffer vs buffer alone, prepared in duplicate, and buffer/MeOH controls showed no SDS rate effect, the half-life being ≈7 h in each case (Table I). First-order kinetics with a high correlation coefficient were observed. The reactions were sampled periodically, extracted, and analyzed by GC using an internal standard and appropriate response factors. Product distributions after ≈3 half-lives (25 h) are given in Table II and structures are shown in Scheme I. Four major alcohols are formed by direct solvolysis: three acyclic, geraniol (2), linalool (3), and nerol (4), and one monocyclic, α-terpineol (5), which could be formed by cyclization of 3 and 4. Two possible conformers of linalyl acetate are shown: **1a**, which yields only acyclic products, and **1b**, which yields both cyclic and acyclic products. There is a small amount of internal return and/or acetate rearrangement as evidenced by geranyl and neryl acetate (6, 7) formation.

A rather large micellar effect on product ratios was found, as shown in Table III. The acyclic/cyclic alcohol

Scheme I

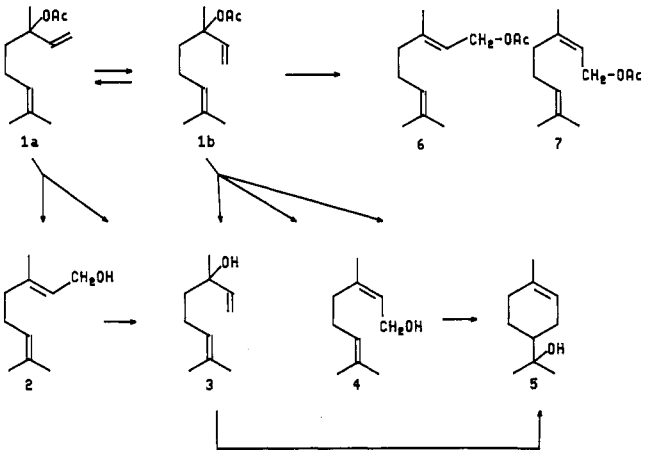


Table III. Effect of SDS on Solvolysis of Linalyl Acetate at pH 3.1: Product Ratios of Acylic/Cyclic Alcohols

time, h	acylic/cyclic alcohol ratio buffer[a]	2% MeOH/buffer	SDS/buffer
3.5	3.13	2.92	
7	2.81	2.75	10.50
25	2.74	2.71	8.52
50	2.70	2.58	6.64
241	2.44	2.36	1.91

[a] Average of duplicate reactions.

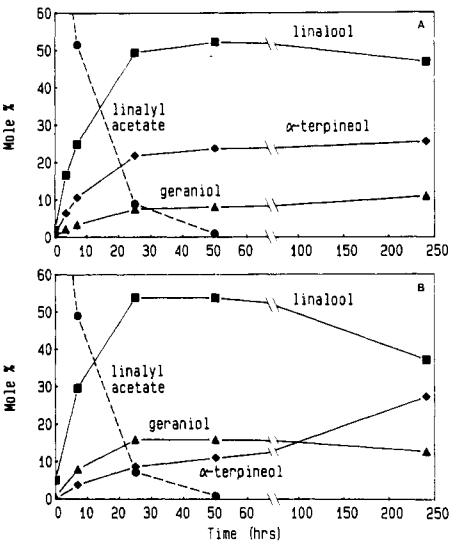
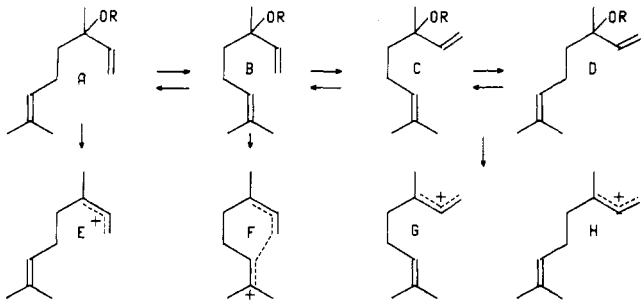


Figure 1. Concentration (mole percent) vs time profiles for linalyl acetate and major reaction products with (A) no SDS (controls), (B) SDS: (■) linalool, (◆) α-terpineol, (▲) geraniol, (●) linalyl acetate.

ratio measured after 25 h was 2.7 without SDS, compared to 8.5 with SDS. The same acyclic/cyclic ratio effect was found at pH 3.5 in 0.07 M citrate/phosphate buffer when linalyl acetate was solvolyzed with and without SDS. As the acetate reaction is completed (after 40 h) and secondary reactions of alcohols predominate, the product ratios with and without SDS converge. The micellar selectivity is further illustrated in Figure 1, which shows the mole percent of linalyl acetate and the major reaction products. During the first 50 h of linalyl acetate solvolysis there is little micellar effect on linalool formation, but the effect on α-terpineol is relatively large, the concentration decreasing from 21 mol % (control) to 9 mol % (SDS). Conversely, the concentration of geraniol more than doubles from 7 mol % (control) to 16 mol % (SDS). Similarly,

Scheme II



nerol formation is 1.5 times greater in SDS (Table II). The formation of geranyl and neryl acetates (**6**, **7**), however, is inhibited in the micelle by a factor of 3 (Table II). Beyond 50 h, there is a slow conversion of geraniol and linalool to α-terpineol only in the presence of SDS, in agreement with earlier observations of Bunton.[6]

Thus, linalyl acetate cyclization is retarded in the micelle while cyclization of linalool and other acyclic alcohols is facilitated by the micelle. These observations can be rationalized via a conformational argument based on the fact that acetates are much less polar than their respective alcohols, and also on measurements[10,11] with geraniol and geranyl acetate in SDS micelles, which indicate geraniol is in the Stern layer while geranyl acetate resides largely in the more hydrophobic area of the micelle. Thus, linalyl acetate should reside more in the water-poor, hydrocarbon-like micellar interior where acyclic conformers (A, C, D; R = Ac) and intermediates (E, G, H) are favored (Scheme II). Conversely, the more polar linalool is near the Stern layer in an area of high water content. This aqueous environment promotes coiling of the hydrocarbon chain of the alcohol and thus favors the cyclic conformer (B; R = H) and intermediate (F) with promotion of cyclization. The increase in α-terpineol from linalool in the micelle may also, at least in part, be a rate effect due to lower pH at the Stern layer as compared to bulk buffer and/or the result of a slow attainment of equilibrium. The argument of chain coiling in aqueous solvents is in accord with van Tamelen's[12] observations on squalene and those of Jiang et al.[13] with shorter chains.

These micellar ratio effects for linalyl acetate are also compatible with an argument based on the lifetime of the carbocation intermediates. Carbocations formed from the acetate would be destabilized in the nonpolar region of the micelle, resulting in less time for rearrangement to the cyclic form F. In contrast, carbocations formed from alcohols could be stabilized in the Stern layer and thus allow for rearrangement to a cyclic intermediate. It has been observed[3] that addition of ClO_4^-, a low charge density anion that increases the lifetime of the carbocation, leads to greater cyclization for the linalyl derivatives.

Solvolysis of Geranyl Acetate. It was of interest to compare the reaction of the primary geranyl acetate (**6**) to the tertiary linalyl acetate (**1**) in the micelle. As the absolute rate of hydrolysis of geranyl acetate is $\approx$ 120 times slower than linalyl acetate, the study was done at pH 2 to achieve a reasonable rate (Table IV). Because of the low pH and slow hydrolysis rate, the reaction resulted in several additional products (**8–10**) that form[9] from hydration of the isopropenyl group (Scheme III).

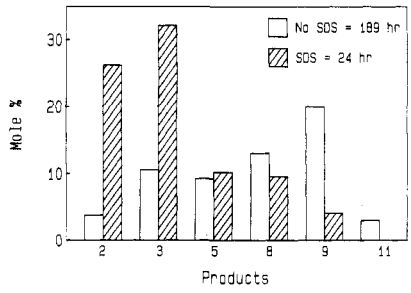


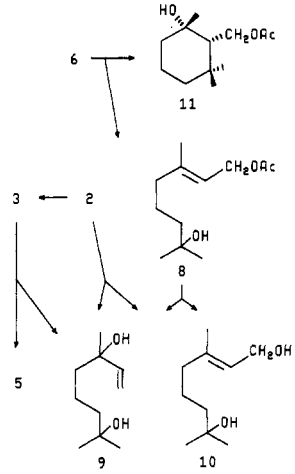
Figure 2. Product distribution for geranyl acetate solvolysis with 10% geranyl acetate remaining: no SDS (controls) vs SDS.

Table IV. Effect of SDS on Geranyl Acetate Solvolysis: Rate Data at 25 °C

kinetic parameters	HCl/citrate buffer reaction 1	HCl/citrate buffer reaction 2	HCl/citrate buffer/3% MeOH	SDS/HCl/citrate buffer
k_{obsd}, h^{-1}	1.20 (10^{-2})	1.20 (10^{-1})	1.12 (10^{-2})	8.57 (10^{-1})
$t_{1/2}$, h	58	58	62	8.1
pH	1.93	1.92	1.91	1.98
k_{abs}[a]	1.02	1.00	0.91	8.2
C_0 (calcd molar concn)	2.4 (10^{-4})	2.4 (10^{-4})	2.8 (10^{-4})	3.1 (10^{-4})
coeff of determ	0.999	0.999	0.999	0.999

[a] $k_{abs} = k_{obsd}$ (h^{-1})/[H^+](mol/L) = L mol^{-1} h^{-1}.

Scheme III



Geranyl acetate was used at a C_0 of 0.24 mM in buffer only, which is just below its solubility limit in this system. Slightly higher concentrations were used in methanol/buffer and SDS/buffer (Table IV). Addition of SDS (38 mM) gave a 7-fold rate increase compared to the no SDS controls (Table IV). This is in contrast to the lack of a rate effect for linalyl acetate. There was good duplication of rates in the two types of controls, buffer vs 3% methanol/buffer, and all gave first-order kinetics as did the SDS reaction.

The product distribution after 90% completion of reaction is very different for SDS vs controls (Figure 2). This distribution difference is due to the relatively large rate effect observed with SDS; after 24 h only 10 mol % of geranyl acetate remains unreacted compared to 80 mol % in the control. With SDS, geranyl acetate is quickly transformed before any appreciable hydration of the isopropenyl group takes place, whereas without SDS, the

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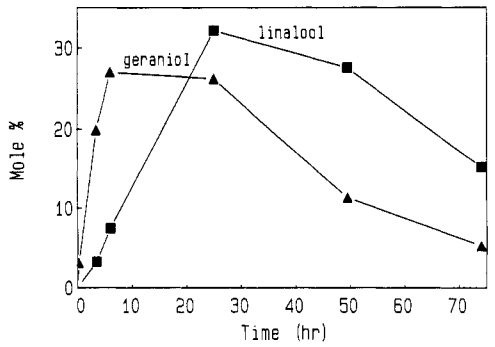
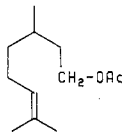


Figure 3. Solvolysis of geranyl acetate (SDS, pH = 2): formation of key products.

acetate is solvolyzed at a rate similar to the reaction of the isopropenyl group. Thus, the use of SDS yields a very different product distribution from that obtained with no SDS, a product distribution that probably cannot be achieved otherwise. In addition, total product recovery is quantitative in SDS, compared to 70% in the control, after 90% completion of geranyl acetate hydrolysis.

While some SDS-induced selectivity may be present, a careful analysis of rate and product data indicates most of the difference in product distribution is due to SDS-induced rate rather than selectivity. One definite exception is the complete lack of cyclic ester **11** in SDS. This is in agreement with our rationale of less coiling for the acetates in the micelle as opposed to buffer only.

The difference in absolute rate and SDS effect between linalyl acetate and geranyl acetate is compatible with a difference in mechanism. While definitive mechanistic studies have apparently not been reported on these two acetates under acid-catalyzed conditions, a difference in mechanism is indicated from literature reports on other esters and from our product studies. The solvolysis of linalyl acetate, a tertiary allylic ester, clearly takes place by alkyl–oxygen ($A_{AL}1$) cleavage.[14] The mechanism for solvolysis of a primary allylic acetate like geranyl acetate is not clear from the literature[15] for our conditions, but evidence presented here indicates it to be predominantly by acyl cleavage ($A_{AC}2$). Our observed absolute rate difference of 120-fold between linalyl and geranyl acetate is compatible with rate differences cited in the literature[15,16] for these two mechanisms, with the slower rate being acyl cleavage, as found. In addition, solvolysis[17] of citronellyl acetate (**12**) under similar conditions gave an absolute rate



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constant of 1.18 L mol^{-1} h^{-1}, very similar to geranyl acetate (Table IV), which indicates no anchimeric assistance to solvolysis by the 1,2 double bond in the latter. Furthermore, our data for geraniol and linalool formation from geranyl acetate in SDS (Figure 3) show fast initial formation of geraniol, as expected from a predominantly acyl cleavage mechanism.

The difference in response to the effect of SDS exhibited by the two acetates could be conceptualized on purely energetic grounds. For linalyl acetate, a rather reactive, strained compound, the ground state would be expected to be close to the transition state in energy, and in accord with the Hammond postulate,[18] SDS would have little or no effect on rate. In contrast, the ground state of geranyl acetate is unstrained, relatively low in energy, and one would expect the transition state to be of considerably higher energy than starting material; thus, the rate would be moderately affected by SDS as is the case in general for acid-catalyzed solvolysis of saturated primary acetates.[19]

In summary, SDS can have a rather large effect on product ratios where there are multiple intermediates of similar energy, as in the case for linalyl acetate and citronellal.[4] For geranyl acetate, SDS can lead to a very different product mixture due to a modest rate effect on this slow reaction.

Experimental Section

Quantitative analyses by GLC were performed on a Varian 6000 (FID) equipped with a 12 ft × $^1/_8$ in. i.d. glass column configured for on-column injection and packed with 5% Triton X-305 on Chromosorb W. H.P. 80–100 mesh. The oven temperature was programmed from 70 to 170 °C at 2 °C/min with 10-min initial hold. A flow rate of ≈35 mL/min of helium was employed. The injector and detector were maintained at 160 and 250 °C, respectively. Capillary GLC analyses were performed with either a J&W, DB-5 or DB-wax (carbowax) fused silica column, 30 m × 0.53 mm (i.d.), 1.5 μm film thickness or 0.32 mm (i.d.), 1 μm film thickness versions. IR spectra were determined on a Digilab FTS-40 GC/FTIR, and MS were determined on a HP-5985 GC/MS equipped with a HP 5840 GC, employing in each case the 0.32-mm (i.d.) versions of the above fused silica capillary columns. Sodium dodecyl sulfate was obtained from Bio-Rad Laboratories and used as received. The SDS purity was checked by a control reaction followed by extraction and GLC, and also by a CMC determination employing conductivity. The linalyl and geranyl acetates, each 96% pure by GLC, were a gift from Union Camp Corp. and were used as received.

Solvolysis of Linalyl Acetate in HCl/Citrate Buffer. A ≈0.05 M HCl/citrate buffer was prepared (0.036 M HCl and 0.015 M sodium citrate). SDS (1.1 g, 3.8 mmol) was added to buffer (0.038 M HCl and 0.015 M sodium citrate), final volume of 100 mL, to yield a 0.038 M solution of pH 3.11. Aliquots (90 mL) of buffer or SDS/buffer were each placed in 100-mL flasks and deaerated with argon. The buffer-only control was run in duplicate (reaction 1, reaction 2; Tables I and II). Linalyl acetate (≈5.4 mg) was added by repeatable syringe using underwater injection to yield a 0.30 mM (theoretical) solution (actual C_0's calcd from rate expression). The methanol/buffer solution was prepared by dissolving the same amount of linalyl acetate in methanol (2 mL) and diluting to 90 mL with buffer. Each sample was stirred, deaerated again with argon, sonicated for 15 min, and placed in a bath at 25 °C with magnetic stirring. The reactions were sampled (10 mL) periodically (Figure 1), and tetradecane in ether added as an internal standard. The samples were extracted with ether (1 × 100 mL; 3 × 50 mL) and washed successively with saturated $NaHCO_3$ (1 × 25 mL), water (1 × 25 mL), and saturated NaCl (1 × 25 mL). Extracts were concentrated to ≈3 mL in a Kuderna–Danish evaporative still and analyzed by packed-column GLC using the internal standard and response factors determined from authentic compounds of known purity.

All GLC determinations were made at least in duplicate, and values were averaged. For the linalyl acetate buffer-only controls the t_0 analysis value was not used due to slow dissolution of the acetate. Reaction products were identified by GC/MS comparison to standard spectra and GC peak enrichment with authentic standards where necessary. Reactions of geranyl acetate (Table IV) were generally carried out as above, and in addition, products

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were identified by GC/FTIR and comparison of IR spectra to those of known compounds kindly supplied by Dr. McHale.[9]

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Supplementary Material Available: Tables of complete composition vs time data for linalyl and geranyl acetate solvolysis under all conditions and structures of minor products (7 pages). Ordering information is given on any current masthead page.

1,3-Dialkyltriazenes: Tautomeric Equilibria and Rates and Products of Decomposition†

Richard H. Smith, Jr.,*,‡,§ Brian D. Wladkowski,‡ Andrew F. Mehl,‡ Michael J. Cleveland,‡ Elizabeth A. Rudrow,‡ Gwendolyn N. Chmurny,∥ and Christopher J. Michejda*,§

Department of Chemistry, Western Maryland College, Westminster, Maryland 21157, and Laboratory of Chemical and Physical Carcinogenesis, BRI-Basic Research Program, NCI-Frederick Cancer Research Facility, Frederick, Maryland 21701

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Unsymmetrical 1,3-dialkyltriazenes, RN=NNHR′, exist as a tautomeric mixture because of rapid proton exchange between nitrogens 1 and 3. Hydronium ion catalyzed decomposition of these triazenes gives rise to a mixture of alkanediazonium ions, RN_2^+ and $R'N_2^+$, and the corresponding primary amines. The objective of this study was to determine the factors that influence partitioning between the two pathways originating from the two tautomers. A series of 1-alkyl-3-methyltriazenes, where the alkyl groups were ethyl, *n*-propyl, *n*-butyl, isopropyl, *tert*-butyl, and benzyl, were prepared. A new, and potentially less hazardous, preparation of low molecular weight alkyl azides was developed. The corresponding symmetrical 1,3-dialkyltriazenes were also prepared. The rates of decomposition in aqueous buffers were measured. The general kinetic behavior suggested that the overall mechanism was specific acid catalysis in glycine buffer, in keeping with previously published data on symmetrical dialkyltriazenes (*J. Am. Chem. Soc.* **1986**, *108*, 3726–3730). The products of the decomposition of unsymmetrical triazenes were determined quantitatively, with particular reference to the alcohols formed by hydrolysis of the diazonium ions, RN_2^+ and $R'N_2^+$. The tautomeric distributions of the unsymmetrical triazenes were determined by NMR in various solvents, and it was found that Lewis base solvents (methanol, THF, acetone) capable of forming a hydrogen bond to the triazene gave very similar distributions, which was markedly different from solvents such as dichloromethane or chloroform. For each triazene, the tautomer in which the larger alkyl group is located on nitrogen 1 was favored. It was assumed that the distribution in water was similar to that observed in methanol. The rates of tautomerization were measured by dynamic NMR methods. Quantitative analysis of the combined data indicated that the unsymmetrical triazenes obeyed the Curtin–Hammett principle. Both the rates of decomposition of the triazenes and the ratios of the products are a function of the rates of decomposition of the conjugate acids of the tautomers and the mole fraction and basicity of the individual tautomers. The analysis also provides a means of predicting the ratios of alkanediazonium ions derived from unsymmetrical triazenes.

Introduction

The synthesis[1,2] and kinetics of proteolytic decomposition of 1,3-dialkyltriazenes,[3] 1,3,3-trialkyltriazenes,[4,5] and 1,3-dialkyl-3-acyltriazenes[6] have been described. The preceding papers on dialkyltriazenes, however, dealt only with those compounds in which the alkyl substituents on N(1) and N(3) were the same (e.g., 1,3-dimethyltriazene (DMT), 1,3-diethyltriazene (DET), etc.). An additional complication arises when unsymmetrical 1,3-dialkyltriazenes are considered, because they exist as pairs of isomers in tautomeric equilibrium (see below).

We have shown previously[3] that the proteolytic decomposition of 1,3-dialkyltriazenes is initiated by a rapid and reversible proton transfer to N(3) and subsequent heterolysis of the protonated triazene to an alkanediazonium ion and an alkylamine. In the case of the unsymmetrical triazenes, the equilibrium distribution of the tautomeric forms may play a significant role in the determination of the rate of reaction and of the direction of heterolysis, which could lead to the formation of two diazonium ions, RN_2^+ and/or $R'N_2^+$ (and the primary amines $R'NH_2$ and RNH_2, respectively).

This paper seeks to study this problem. A series of unsymmetrical 1-alkyl-3-methyltriazenes were prepared together with the corresponding symmetrical 1,3-dialkyltriazenes. The rates of decomposition of these triazenes were determined in aqueous buffers; the yields of the alcohols, formed from the hydrolysis of the diazonium ions, were measured; and the tautomeric equilibria and the rates of proton transfers between N(1) and N(3) were measured

† This paper is dedicated with best wishes to Professor R. Preussmann, German Cancer Research Center, Heidelberg, on the occasion of his 60th birthday.

‡ Department of Chemistry, Western Maryland College.

§ Laboratory of Chemical and Physical Carcinogenesis, BRI-Basic Research Program, NCI-FCRF.

∥ Chemical Synthesis and Analysis Laboratory, PRI, NCI-FCRF.

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