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Steric Effects in Homogeneous Gas-Phase Reactions. Pyrolysis of Isopropyl Esters

Grant Gill Smith,* Linda Mutter,[1] and G. Peter Todd[1]

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322

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Absolute reaction rate constants have been determined in the pyrolysis of 18 isopropyl alkanoates to acids and propene in a very carefully deactivated stainless steel static reactor. Trisubstitution by alkyl groups at the α position of the acid moiety showed a small, but readily measurable, rate of acceleration. Substitution at the β position had no effect on the rate of pyrolysis. This rate acceleration was reflected in the entropy of activation. α-Phenyl and α-chloro substituents influence pyrolysis rates more than α-alkyl substituents and at least with the chloro substituent the effects are a combination of both steric and electronic.

The pyrolysis of esters, when studied in a very carefully deactivated reactor, has been demonstrated to be a homogeneous, first order, unimolecular reaction proceeding through a converted cyclic transition with a degree of charge separation between the oxygen and carbon. Removal of the β hydrogen is also part of the rate-determining step. The mechanism which has been proposed[2] explained all available data excepting some rearrangements which likely were not gas-phase reactions but surface-catalyzed reactions. Refinements to this mechanism have been presented by others.[3] There are, no doubt, many studies on ester pyrolysis which were thought to be gas-phase reactions but were carried out in unseasoned reactors, e.g., dropping the ester through a clean glass tube, which most likely were not homogeneous gas-phase reactions but rather were surface-catalyzed reactions resulting in different product ratios, rearrangements, and faster reaction rates than are found under strictly gas-phase reactions conditions.

There have been many studies dealing with the electron influences on the rate of pyrolysis,[4a] but only a very few which have dealt specifically with steric influences on pyrolysis rates. Studies of steric effects in the acid moiety are very limited. Tinkelenberg et al. included some steric effect studies in their paper on the polar nature of β-elimination reactions.[4b] Effects of electronic changes in the acid portion are known to be not nearly as influential as they are in the alkyl portion. This paper reports a study of changes in steric effects in the acid portion on the ease of ester pyrolysis and a report of some electronic effects studies.

Steric effects in unimolecular homogeneous gas-phase pyrolysis of esters are not expected to be pronounced and certainly not as great as found in bimolecular reactions such as found in mineral acid catalyzed esterification of carboxylic acids. However, a measure of the effects, if present, would reveal some interesting aspects about gas-phase pyrolysis mechanisms and the nature of steric interactions as well. In homogeneous gas-phase reactions, all solvent effects are excluded.

The absolute rate constants have been determined for 18 isopropyl esters in which the extent of substitutions at the α and β positions have been varied. The electronic effects by different alkyl groups are very similar. Therefore, any change in rate will reflect steric interactions. Although the high temperatures used in pyrolysis of esters (~378 °C) minimize substituent effects, small effects are readily detectable within experimental error when studies are made in a carefully deactivated reactor. Activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) were determined for the two esters (VII and VIII, Table I)

Table I. Synthetic and Pyrolysis Kinetic Data for Isopropyl Carboxylates

Registry no.	Isopropyl ester	Formula	Bp, °C (mm)	n^{20}D	Purity, %	Yield, %	$k \times 10^5$ at 651 K	$k_{alkanoate}/k_{acetate}$
108-21-4	I acetate[a]	$CH_3COOCH(CH_3)_2$	85 (640)	1.3783	98.1	30	5.93 ± 0.17	1.00
637-78-5	II propionate[b]	$CH_3CH_2COOCH(CH_3)_2$	108 (640)	1.3865	98.3	40	6.10 ± 0.20	1.03
638-11-9	III butyrate[c]	$CH_3(CH_2)_2COOCH(CH_3)_2$	125 (640)	1.3930	99.6	55	5.93 ± 0.27	1.00
18362-97-5	IV valerate[d]	$CH_3(CH_2)_3COOCH(CH_3)_2$	147.5 (640)	1.4002	97.3	7.2	5.97 ± 0.07	1.01
2311-46-8	V caproate[e]	$CH_3(CH_2)_4COOCH(CH_3)_2$	177 (640)	1.4072	96.3	18	6.03 ± 0.27	1.02
617-50-5	VI isobutyrate[f]	$(CH_3)_2CHCOOCH(CH_3)_2$	120.8 (640)	1.3873	98.6	62	6.80 ± 0.20	1.15
5129-36-2	VII pivalate (trimethylacetate)[g]	$(CH_3)_3CCOOCH(CH_3)_2$	125 (640)	1.3882	98.7	21	7.68 ± 0.32	1.30 (1.40)[h]
60498-66-0	VIII β,β-dimethylbutyrate (*tert*-butylacetate)[i]	$(CH_3)_3CCH_2COOCH(CH_3)_2$	147 (640)	1.4025	98.2	61	5.95 ± 0.19	1.01
5129-47-5	IX α-ethylbutyrate[j]	$CH_3—CH_2CH(CH_2CH_3)COOCH(CH_3)_2$	163 (640)	1.4033	96.8	30	6.97 ± 0.17	1.18
6639-15-2	X α-methylvalerate[k]	$CH_3(CH_2)_2CH(CH_3)COOCH(CH_3)_2$	171 (640)	1.4021	97.3	29	6.88 ± 0.24	1.16
60498-67-1	XI α-propylvalerate[l]	$CH_3(CH_2)_2CH(CH_2CH_2CH_3)COOCH(CH_3)_2$	32 (0.1)	1.4109	97.5	14	6.89 ± 0.30	1.16
4861-85-2	XII phenylacetate[m]	$PhCH_2COOCH(CH_3)_2$	65 (0.3)	1.4875	99.4	29	8.13 ± 0.13	1.37
60498-68-2	XIII diphenylacetate[n]	$Ph_2CHCOOCH(CH_3)_2$	132 (0.3) (mp) 42–43		>99	52	11.2 ± 0.07	1.88
22767-95-9	XIV hydrocinnamate (β-phenylpropionate)[o]	$PhCH_2CH_2COOCH(CH_3)_2$	87 (3)	1.4868	99.3	69	7.37 ± 0.07	1.24
18060-77-0	XV crotonate[p]	$CH_3CH=CHCOOCH(CH_3)_2$	140 (640)	1.4221	98.7	9	7.1 ± 0.20	1.20
60512-85-8	XVI *trans*-cinnamate[q]	$PhCH=CHCOOCH(CH_3)_2$	98 (0.6)	1.5450	98.1	51	8.13 ± 0.37	1.37
105-48-6	XVII chloroacetate[r]	$ClCH_2COOCH(CH_3)_2$	142 (640)	1.4193	98.9		10.6 ± 0.40	1.79
17640-21-0	XVIII methoxyacetate[s]	$CH_3OCH_2COOCH(CH_3)_2$	152 (640)	1.4010	95.4	55	6.87 ± 0.27[t]	1.16

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which show how methyl substituents at the α position alter activation parameters compared to methyl substituents at the β position.

Experimental Section

Materials. The isopropyl esters were synthesized from commercially available acids by two different methods. Method I[5] was a simple esterification using dry hydrogen chloride gas (3–4 N solution) in a 3 molar excess of 2-propanol. Refluxing was continued from 2 to 5 days. The mixture was taken up in chloroform and then extracted with a saturated aqueous solution of sodium bicarbonate to remove the organic and inorganic acids. The crude ester–chloroform solution was dried overnight ($MgSO_4$) and the volatile solvent removed on a rotary evaporator. The esters were distilled through a 24-in. spinning band column and the purity determined by a Hewlett-Packard 5830A digital computer controlled flame ionization gas chromatograph (20 in. 10% UC-W982 0.125 in. stainless steel column). Characterization was by refractive index, NMR, and mass spectral analysis. Esters I–VII, IX, and XII–XVIII were prepared by method I. Owing to the expense and small working quantities of the other acids, the following method was used to prepare esters VIII, X, and XI.[6] Millimolar quantities of the acids were dissolved in 11 molar excess of benzene, a four times excess of trifluoroacetic anhydride, and a 10 molar excess of 2-propanol. After refluxing overnight, the solution was washed with 10% sodium hydroxide solution, dried over magnesium sulfate and fractionally distilled. The yield, in every case, was sacrificed for purity. The data on the esters are reported in Table I.

Kinetics. Kinetic data were obtained by monitoring pressure changes in a constant-volume static reactor which has been previously described.[7] The reaction temperature (651.0 K) was determined by in situ thermocouples calibrated against a platinum resistance thermometer. Thermolyses were carried out at initial reactant pressures in the range of 250–400 Torr. With selected esters cyclohexene was added to check for radical reactions. Reaction rates were invariant with initial pressure and/or additive. The reaction chamber was well seasoned by the thermolysis of multiple injections of 3-butenoic acid at 680 K.[8] The absence of surface catalysis was ascertained by the thermolysis of 1-phenylethyl acetate which gave first-order kinetics of high precision (±1–2%) in agreement with reported values.[9] The rate constants, standard deviations, and correlation coefficients were computer calculated. The reaction rate constants for each of the esters are shown in Table I. At least three rate determinations were made on each ester. The maximum deviation from the average never exceeded 4.4%. The reaction proceeded to 80% completion without any complications or subsequent decompositions. The products were the acid and propene.

Discussion

There is no observable effect on the rate of pyrolysis with increasing chain length within experimental error. The relative rate constants ($k_{carboxylate}/k_{acetate}$) from acetate through caproate are 1.00:1.03:1.00:1.01:1.02, respectively. These results demonstrate that one alkyl substituent at the α or β position, regardless of its size within the range studied, has no effect, sterically or electronically, on the rate of pyrolysis. This is a surprising result as it is generally considered that larger molecules fragment more readily than smaller ones.[10]

The second and third methyl substituent at the α position, however, shows a steric acceleration effect. The relative rates in the pyrolysis of isopropyl esters are acetate (I):propionoate (II):isobutyrate (VI):pivalate (trimethylacetate) (VII) 1.00:1.03:1.15:1.30. These are not marked effects but are beyond experimental error. Cross and Stimson did not observe any difference in the rate of pyrolysis between ethyl acetate and ethyl trimethylacetate.[11] Substituent effect in primary esters are less pronounced than in secondary and tertiary esters, and therefore they are more difficult to detect.

The lack of any influence by alkyl branching at the β position in the pyrolysis of isopropyl carboxylates is forcibly demonstrated by the tabulated results given in Table II. If isopropyl isobutyrate is selected as a logical standard it is clearly evident that substitution by one or two methyl or ethyl substituents at the β position has absolutely no influence on the rate of ester pyrolysis. This is further emphasized by comparing the results when three methyl substituents are examined at these two positions.

Table II. Effect of Alkyl Branching at the β Position in Alkanoate Pyrolysis[a] R-COOCH(CH_3)$_2$

R	$K \times 10^3$	Maximum deviation	Average deviation	Ratio
H_3C>CH H_3C	6.80	±0.20	±0.10	1.00
CH_3CH_2>CH CH_3CH_2	6.97	±0.17	±0.11	1.03
CH_3>CH $CH_3(CH_2)_2$	6.88	±0.24	±0.18	1.01
$CH_3(CH_2)_2$>CH $CH_3(CH_2)_2$	6.89	±0.30	±0.22	1.01

[a] 651 ± 0.1 K.

Placing three methyl substituents at the α position has perceptibly more effect on the rate of pyrolysis than three methyl substituents at the β position. Isopropyl pivalate (isopropyl trimethylacetate) (VII) pyrolyzed 1.3 times faster than isopropyl β,β-dimethylbutyrate (isopropyl *tert*-butylacetate) (VIII). Tinkelenberg et al. reported 1.4 for the ratio of cyclohexyl trimethylacetate/cyclohexyl acetate. These comparisons of effects of the α and β position demonstrate that steric effects in ester thermolysis are greater at the α position than at the β position.

Likewise, a phenyl substituent increases the rate of pyrolysis more at the α position than at the β position. The ratios for the isopropyl ester are acetate (I):β-phenylpropionoate (XIV):phenylacetate (XII):diphenylacetate (XIII) 1.0:1.24:1.37:1.88. The effect is primarily steric since the phenyl substituent causes only a minor electronic effect being electromerically insulated from the reaction site by a methylene group. Electronic changes in the acid portion of the ester are known to cause only a minor influence on ester pyrolysis.[12] The effect of a C=C double bond on ester pyrolysis was studied by comparing the absolute reaction rate constants in the pyrolysis of isopropyl esters of *n*-butyric acid (III), *trans*-crotonic acid (XV), and *trans*-cinnamic acid (XVI). Their relative rates are 1.00:1.20:1.37, respectively. Again the effect is not large but well beyond experimental error and clearly shows that unsaturation increases the rate. Here electronic effects could be relayed to the active site and would be expected to have an effect. Kairaitis and Stimson[13] reported a similar result. Their data, taken at 410.4 °C (683.5 K), for ethyl butyrate (1.61×10^{-3}) and ethyl *trans*-crotonate (1.83×10^{-3}) gave a ratio of 1.14. Primary esters are not expected to show as large a substituent effect as secondary esters.

α-Chloro substituents are more effective on the rate of pyrolysis of esters than are α-alkyl or α-aryl substituents. The rate of pyrolysis of isopropyl chloroacetate (XVII) was 1.79 times faster than the rate for isopropyl acetate (I). Similar results are reported for *tert*-butyl esters although it is difficult to place a number on the extent of influence. Several values have been reported for the rate constant in the pyrolysis of *tert*-butyl acetate.[14] When the reported values, obtained at different temperatures, were recalculated to 650 K, they ranged from 243×10^{-3} to 615×10^{-3}. Using Emovon and Maccoll's[15] values for *tert*-butyl acetate (496×10^{-3}), and Emovon's values[16] for *tert*-butyl α-chloracetate (1925×10^{-3}) and *tert*-butyl α,α-dichloroacetate (4430×10^{-3}) the relative rates are 1.00:3.9:9.0, respectively. Substituent effects are expected to be greater with tertiary esters than with secondary and primary esters and indeed they are. With chloro substit-

uents at the α position, electronic and steric effects are combined to magnify the substituent influence. An α-methoxy substituent and α-unsaturation have greater acceleration effects on pyrolysis than do α-alkyl substituents but not as great an effect as α-phenyl and α-chloro substituents.

Kooyman et al.[4b] reported a ratio of cyclohexyl trifluoroacetate/cyclohexyl acetate of 19. This very strong effect at the α position of the acid is very significant and most likely is polar rather than steric. The data for isopropyl trichloroacetate are not available but it would appear from the increased rates due to one α-chloro substituent that three chloro substituents would cause an effect even greater than three fluoro substituents because of the combination of both steric and electronic effects.

In summary, therefore, these results demonstrate that substituent effects are more important at the α than at the β position in the acid moiety of esters on their pyrolysis. Multiple branching at the α position by alkyl groups causes a greater steric acceleration effect (compound VII) than similar substitution at the β position (compound VIII).

It is now clear that in pyrolysis, electron-withdrawing groups or electron-releasing groups in the acid moiety at the α position cause rate accelerations.

This suggests that the effects by α-aryl and α-aryl are more than electronic. We proposed that steric effect raise the ground state of the ester effectively reducing the activation free energy. Further evidence to support this concept was found by comparing the activation parameters of the isopropyl esters of trimethyl acetate (VII) and *tert*-butyl acetate (VIII). The entropy of activation ($\Delta S^{\ddagger}$) for VII, where the three methyl groups are located at the α position, showed a less negative value than β-methyl substituent. $\Delta S^{\ddagger}$ for VII was -0.25, while $\Delta S^{\ddagger}$ for VIII was -4.7. The rate ratio for the pyrolysis of these two esters was 1.3. From this we conclude that the more sterically hindered ester (VII) is held in a favorably conformation leading to the cyclic transition state. This supports the well-accepted mechanistic concept.[2] The enthalpies of activation for VII and VIII were found to be 45.0 and 42.5 kcal/mol, respectively. Wigfield and Phelps reported recently[17] that the major component of the free energy barrier in the sodium borohydride reduction of hindered ketones, which alters reactivity, is entropy.

Although ester pyrolysis and ester formation are very different processes, it is interested to compare the two reactions sterically. Newman[18] proposed that steric effects at the β carbon in acid esterification was greater than at the α carbon. However, Sniegoski[19] has challenged Newman's interpretation of the data.

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Electrocyclic Synthesis of 5,6- and 7,8-Dihydroquinolines and 5,6- and 7,8-Dihydroisoquinolines

Bruce Irwin Rosen and William P. Weber*

Department of Chemistry, University of Southern California, Los Angeles, California 90007

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The gas-phase pyrolysis of a number of 1-(ω-pyridinyl)-1,3-butadienes (650 °C, 1 mm, and a contact time ~0.1 s) has been studied. The following results were obtained: 1-(α-pyridinyl)-1,3-butadiene yields 5,6-dihydroquinoline, 1-(β-pyridinyl)-1,3-butadiene yields 5,6-dihydroisoquinoline (35%) and 7,8-dihydroquinoline (65%), and 1-(γ-pyridinyl)-1,3-butadiene yields 7,8-dihydroisoquinoline. Analogous results were obtained on pyrolysis of 1-methyl-1-(ω-pyridinyl)-1,3-butadienes and 1-(6'-methyl-2'-pyridinyl)-1,3-butadiene. The structures of these 5,6- and 7,8-dihydroquinoline and 5,6- and 7,8-dihydroisoquinoline isomers were determined by spectral methods, dehydrogenation to the parent aromatic heterocycle, and in the case of 5,6- and 7,8-dihydroquinoline by use of Eu(fod)$_3$ NMR shift reagent. The mechanism of this reaction is discussed.

We should like to report a general synthesis of 5,6- and 7,8-dihydroquinolines (I, II) and 5,6- and 7,8-dihydroisoquinolines (III, IV) based on joining onto a pyridine ring a specific partially reduced aromatic ring. The critical ring closure reaction onto the pyridine nucleus is an electrocyclic reaction.[1] A communication reporting this reaction appeared 5 years ago.[2] The inaccessibility of I, II, III, and IV isomers convinced us that a detailed study to improve regioselectivity and yields and to determine the scope of this reaction was warranted.

The synthesis is based on the gas-phase pyrolysis of the appropriate 1-(ω-pyridinyl)-1,3-butadiene. Pyrolysis of 1-(γ-pyridinyl)-1,3-butadiene (V)[3] in the gas phase at 650 °C