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GAS CHROMATOGRAPHIC REACTOR STUDY OF THE KINETICS OF METHYLCYCLOPENTADIENE DIMER DISSOCIATION

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SUMMARY

The application of the gas chromatographic column as a chemical reactor was examined further. Specifically the kinetics of the dissociation of three reactive methylcyclopentadiene dimers were studied over a temperature range of 180–210°. The three isomers were separated from a commercial mixture and purified by preparative chromatography. Problems related to the preparative chromatography of such reactive compounds are discussed.

Both gas phase and liquid phase rate constants were determined using the "inert standard" method. The product curve obtained in the course of the dissociation of the dimers in a gas chromatographic reactor during a single run also can be used to estimate the rate constant for the reaction. The method appears general, but must be applied with some knowledge of the relevant physical and chemical processes in the reactor.

Solvent effects on the reaction were studied by determining rate constants in several liquid phases including a silicone, a poly(phenyl ether), an alkane and a polyester. Results can be compared to an earlier study from our laboratories on dicyclopentadiene [*J. Phys. Chem.*, 76 (1972) 2159]. The effect of the position of the methyl groups on the dicyclopentadiene ring and ring stability is also discussed.

INTRODUCTION

Methylcyclopentadiene isomers frequently occur in the thermal cracking of petroleum and similar hydrocarbon fractions. At temperatures below 125° they readily associate to give a mixture of dimeric isomers. Here we describe a gas chromatographic reactor study of the kinetics of dissociation of the dimers as well as some of the problems of preparative gas chromatographic separation of the dimers. We were particularly interested in further investigation of the application of the gas chromatographic reactor[1,2] and in the possible use of the dimers as model compounds for the study of the preparative chromatography of thermally labile compounds. The limited number of earlier studies of the kinetics of dissociation of the methylcyclopentadiene dimers

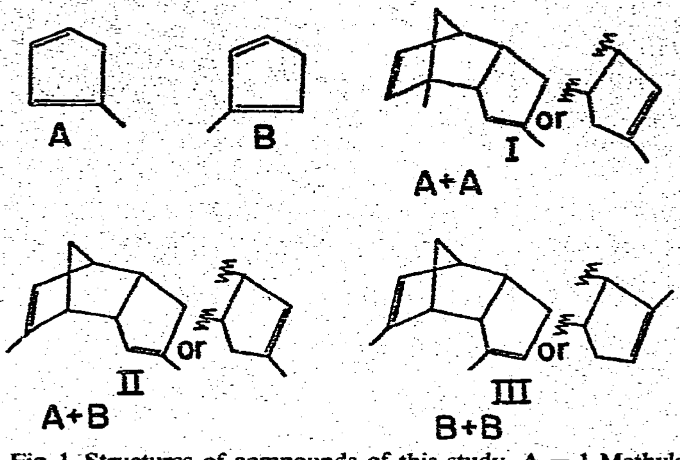

Fig. 1. Structures of compounds of this study. A = 1-Methylcyclopentadiene; B = 2-methylcyclopentadiene; postulated structures for dimers I, II and III indicated (see text).

have used the isomeric mixtures[3,4], and it is only the access to preparative gas chromatography which made the present study of the dissociation of the individual isomers possible.

While three isomers of methylcyclopentadiene can be isolated, it are the 1-methyl (A) and 2-methyl (B) forms shown in Fig. 1 which occur predominantly[5]. These forms associate to give the dimers indicated in Fig. 1. The molecules reacting to give specific dimers were identified by Csicsery[5] through the use of known mixtures of starting monomers and other evidence. The tentative assigned structures are supported by nuclear magnetic resonance evidence (see Experimental). The dimers are believed to exist mainly in the reactive *endo*-form[5]. A preparative chromatogram for a large sample of commercial dimeric mixture is shown in Fig. 2 with the indicated composition and cut points.

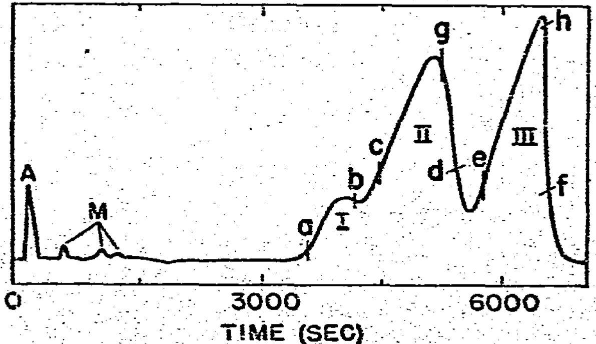

Fig. 2. Typical preparative chromatogram for the separation of dimer isomers from commercial methylcyclopentadiene dimer mixtures. Column, 366 cm × 0.95 cm O.D., Silicone DC-550–Gas-Chrom R (20:80). For non-reactive materials, typical cuts would be made as follows: a–b (dimer I); c–d (dimer II); e–f (dimer III). For reactive materials here, cut points are c–g (dimer II) and e–h (dimer III) to eliminate trapping of reaction products. A = Air; M = impurities; T = 116°; flow-rate, 265 ml/min; ΔP = 72.4 cm.

The chromatographic reactors employed here are gas–liquid chromatographic columns with pulse injection[1,2]. Both reaction and separation of product from reactant are initiated immediately upon introduction of a reacting sample to the column and continue throughout the passage of the reactant through the column. Product dilution and separation from the reactant peak minimizes the effect of any reverse reaction. The chromatographic reactor has been discussed extensively earlier. It can be distinguished from the common micro-reactor in the incorporation of the separation feature in the column. The dissociation or retro Diels–Alder reaction occurs in both the gas and the liquid phase[3,6] and is readily amenable to study in the chromatographic reactor.

EXPERIMENTAL

Preparative work

The preparative chromatograph used for this study was constructed by modifying a Thelco Model 18 forced convection oven. The injector incorporated a Hamilton Model 86800 flash vaporization unit. The column effluent was passed through a stream splitter to give a small detector stream while the main portion was diverted to the trapping system. The detector was a Gow-Mac 470 thermistor cell. The trapping tubes were of a "J" shape instead of the frequently used "U" tubes. The extension of the inlet leg seemed to make the traps more effective.

The columns used for all preparative separations were constructed from 0.95-cm-O.D. stainless-steel column with Silicone DC-550–Gas-Chrom R (20:80) (Applied Science Labs., State College, Pa., U.S.A.) packing. The packing was a 30–40 mesh cut. The optimum flow-rate was determined by a Van Deemter analysis to be about 270 ml/min at a temperature of 110° for a 366-cm column. Samples were trapped in the "J" tubes immersed in a dry ice–acetone bath.

Analyses of trapped fractions were performed on a Carle Model 6500 chromatograph with an aluminum column (183 × 0.3 cm), packed with 20% Silicone DC-550–Gas-Chrom R (60–80 mesh). Impure fractions were recycled through the preparative unit.

Structure assignment

To identify further the structures of the dimeric isomers, nuclear magnetic resonance (NMR) spectra were obtained for $CDCl_3$ solutions of each dimer on a Varian EM-360 spectrometer. The NMR spectrum of dimer I indicates the structure to be 1,4- or 4,7-dimethyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene. The NMR spectrum of dimer II indicates either 4,9- or 4,8-dimethyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene. From the spectral data of dimer III the structure appears to be either 3,9- or 3,8-dimethyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene. Further elucidation of structures is difficult from NMR spectra alone.

Chromatographic reactor

The reactor is a modified version of an earlier model, described elsewhere[1]. The horizontal 25-cm × 91-cm cylindrical air-bath is located inside a 36-cm × 36-cm × 91-cm aluminum box. Marinite strips were bolted to a 20-cm-diameter copper cylinder inside the oven on which nichrome heating wire was non-inductively wound. A Model

703 Torrington blower powered by a 1/3-hp. motor circulated the air inside the oven by pulling air up the inner cylinder and pushing it through the annular space. The air inside the inner tube was exchanged at a rate of 2.7 times/sec.

The temperature was controlled by switching an external resistor in and out of the nichrome heating wire circuit which operates at constant voltage. The temperature was sensed by a nickel resistance thermometer and was controlled to ±0.03° during the course of an experiment. The oven temperature was measured by a deep immersion thermometer, which was calibrated against an NBS thermometer, and was corrected for the spatial temperature variation inside the oven.

The detector was a Gow-Mac Model 460 thermal conductivity cell with tungsten filaments with a Gow-Mac Model 40-001 power supply. The helium carrier gas passed into the oven through the reference side of the detector before it mixed with the sample in the Carle Model 3510 on-column injector.

Columns

Four different liquid phases were used in this study. All were 20:80 liquid phase 60–80 mesh Gas-Chrom Q (Applied Science Labs.), the most inert packing of which we were aware. The columns were made with 304 stainless-steel (0.49 cm I.D.) tubing. Column lengths ranged from 122–244 cm. About 0.8 g of packing/10 cm was used. The columns were Silicone DC-550 (Anspec, Ann Arbor, Mich., U.S.A.), 183 cm; 6-ring poly(phenyl ether) (Anspec), 183 cm; hexatriacontane (Humphrey, North Haven, Conn., U.S.A.), 244 cm (dimers I and II, 180°), and 122 cm for all others; phenyldiethanolamine succinate (Anspec), 244 cm.

Kinetic measurements

The correction of the reactant area for product interference is described elsewhere. Areas were measured with a recorder equipped with a disc integrator (6000 counts per minute at full scale deflection). Other procedures common in chromatography have been described[1,7,8].

PREPARATIVE CHROMATOGRAPHY OF REACTIVE COMPOUNDS

Most compounds can be separated and purified by preparative chromatography with little effort. Once the proper stationary phase and operating conditions have been identified, even partially resolved materials are readily purified. In fact, operating conditions frequently are adjusted to allow peaks to overlap, since such conditions (*e.g.*, higher temperature and flow-rate) may be most conducive to high throughput[9]. However, in some circumstances overlap is indicative of complicating reaction in the column rather than a failure to attain conditions for resolution. Clearly, if product peaks elute with adjacent peaks on the column, separation is complicated.

For this kinetic study, it was necessary to separate the dimers of Fig. 1 from a commercial mixture. Although dimer I, resulting from 1-methylcyclopentadiene, occurred in comparatively small amounts, its limited reactive nature allowed simple preparative separation. Analysis of the other dimers, collected in a conventional manner, showed both to be followed by impurities, apparently due to isomerization.

Verification of chemical reaction is illustrated by the preparative chromatograms of Fig. 3. Fig. 3a illustrates the chromatogram obtained from an untreated

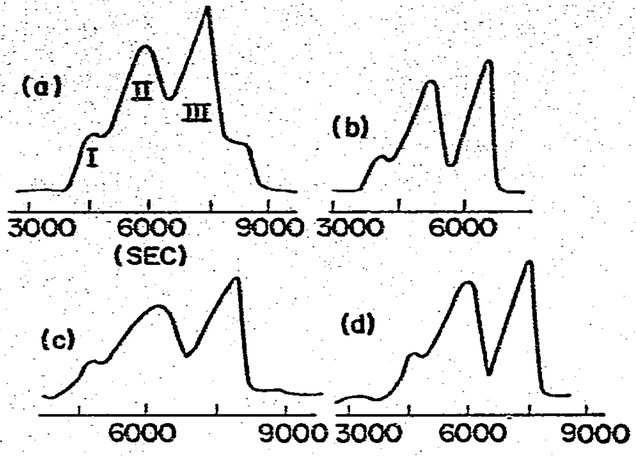

Fig. 3. Preparative chromatography of a dimer mixture showing the effect of sample origin and column treatment on the production of non-reactive materials. (a) Untreated column—Supplier A, column 183 × 0.95 cm O.D.; (b) Supplier A, column 366 × 0.95 cm O.D., after several column treatments; (c) Same column as (b)—Supplier B, after several preparative runs; (d) Same as (c), except injection follows column treatment. All columns Silicone DC-550–Gas Chrom R (20:80). Operating conditions (a) $T = 120°$; Flow-rate, 126.7 ml/min; $\Delta P = 18.9$ cm; (b) $T = 116°$; flow-rate, 264 ml/min; (c) $T = 113°$, flow-rate, 263 ml/min; (d) Same as (c); ΔP for b–d = 72.4 cm.

preparative column, while Fig. 3b shows the chromatogram obtained with the mixture (Aldrich, Milwaukee, Wisc., U.S.A.) after a longer column has been treated with a commercial silylating agent (Silyl 8; Pierce, Rockford, Ill., U.S.A.). Fig. 3c illustrates the deterioration of the packing surface after several preparative runs with another commercial sample (K & K Labs., Plainview, N.J., U.S.A.), while Fig. 3d shows the effect of additional surface treatment of the column on separation. The elimination of the peak following III and the improved resolution of II and III is apparent; evidently both effects stem from surface hydroxyl catalyzed reaction on the column. To minimize the effect of any isomerization of reactive dimers II and III, the trapping schedule of the legend of Fig. 2 was finally adopted. Analytical chromatography showed it to be satisfactory. Columns utilizing much more expensive silylated commercial Gas-Chrom Q showed minimal surface catalysis at higher temperatures.

THEORY

In the gas chromatographic reactor (GCR), concerted reaction and separation processes take place throughout the chromatographic column. We have discussed such reactors extensively on a number of occasions[1,2,7]. The first-order dissociation reactions of interest here are particularly suited for the GCR application because of the ease of separation of products from reactants, thus minimizing the effect of any reverse reaction or tendency for side reaction.

The hypothetical reactor chromatogram is realized in practice, as one can see by examining Fig. 4d for dissociation of dimer III, for example. The tailing of the product peak into the reactant peak distinguishes this chromatogram and similar ones from conventional chromatograms, where only separation takes place. The trailing product area can be approximated by a ramp function, as we have described[1,2,7]. The method for approximating the amount of product contributing to the emerging reactant peak with a ramp function is also indicated in Fig. 4d. The amount of material reacted can be measured by reference to some inert material present in constant concentration in the original reactant solution.

There are a number of techniques for obtaining rate constants from reactor chromatograms. We will be concerned with only two here. One is the "inert standard" method, which we use for obtaining the most accurate data[1]. Because of the possibility of obtaining a good approximation of a rate constant from a single chromatogram, we also describe the "product curve" method[2].

Inert standard method[1]

In this approach, a continuous model of a homogeneous column is combined with a material balance on a reactant pulse which is passing through the column[1,10,11]. When the differential equation which results is solved, the reactant concentration can be related to the position in the column, x, and time, t. Relationships can then be obtained to allow the calculation of first order rate constants. The treatment assumes reaction in both gas and liquid phases. This occurs for the reactive compounds of interest here.

Each species of the mixture introduced to the column is partitioned between the gas and liquid phase and transported by the carrier gas. With rapid mass transfer between phases and a linear adsorption isotherm[1,7], the partition coefficient, K, can be defined by

$$K = C_l/C_g \tag{1}$$

where C_l is the concentration of any species in the liquid phase and C_g the concentration of that species in the gas phase. K is a function of temperature. Small sample size (0.4 μl), even as a pulse, assures minimal heat effects from solution and reaction processes.

If the reactor column is operated in a region where diffusional effects are not important, a material balance on a differential element of the column where a homogeneous first order reaction takes place in both phases yields

$$f_l\left(\frac{\partial C_l}{\partial t}\right)+f_g\left(\frac{\partial C_g}{\partial t}\right) = -f_g\left(\frac{\partial\,[u(x)\,C_g]}{\partial x}\right) - f_g\,k_g\,C_g - f_l\,k_l\,C_l \tag{2}$$

where f_g and f_l are volume fractions of the gas phase and the liquid phase, respectively, $u(x)$ is the linear velocity of the carrier gas at distance x from the column inlet, and k_l and k_g are first order homogeneous rate constants for the indicated phases.

The boundary and initial conditions are

$$C_g(0,t) = \varphi(t); \quad C_g(x,0) = 0 \tag{3}$$

$C_g(x,t)$ is the concentration at point x and time t in the gas phase. $\varphi(t)$ is an arbitrary input function.

As described elsewhere[1,2,12,13], eqn. 2 is solved with the aid of Laplace transforms and the boundary and initial conditions to give $C_g(x,t)$. Thus, concentrations at the column inlet ($x = 0$) are known, and concentrations at the outlet ($x = L$) can be calculated. Upon integration of both inlet and outlet concentrations over appropriate periods of time, the weight of reactant injected, W_{in}, and emerging from the column, W_{out}, can be calculated[1,2]. For a bounded input

$$\frac{W_{\text{in}}}{W_{\text{out}}} = \exp\,(\beta t_g), \text{ where } \beta = \frac{f_g k_g + f_l k_l K}{f_g} \tag{4}$$

$$\frac{W_{\text{in}}}{W_{\text{out}}} = \exp\,(k_g t_g + k_l t_l) \tag{5}$$

where t_g is the time spent in the gas phase and t_l is the time spent in the liquid phase Since

$$t_l = K t_g \frac{f_l}{f_g} \tag{6}$$

and since t_g/t_l is constant for a given column and temperature, eqn. 5 can be rewritten as

$$\frac{W_{\text{in}}}{W_{\text{out}}} = \exp\,(k_{\text{app}} t_l) \tag{7}$$

where

$$k_{\text{app}} = k_l + k_g \frac{t_g}{t_l} \tag{8}$$

Eqn. 5 is independent of the input pulse wave form. Since the area under a reactor chromatogram peak is proportional to the total weight of the corresponding compound as it passes through the detector

$$\ln\left(\frac{A_R^0}{A_R}\right) = k_{\text{app}} t_l \tag{9}$$

where A_R is the area under the emerging reactant peak and A_R^0 is the area of the inlet reactant peak if the detector had been placed at the inlet to the column. Inclusion of an inert compound in the reactant mixture produces a peak with an area (A_I)[1,2]. Adding ln (A_I) to both sides of eqn. 9 and rearranging gives

$$\ln\left(\frac{A_I}{A_R}\right) = k_{\text{app}} t_l + \ln\left(\frac{A_I}{A_R^0}\right) \tag{10}$$

The initial area ratio A_I/A_R^0 is the same for all samples of the same reaction mixture. A_R, A_I and t_l are measured readily. In a reactor column where t_g is very small relative to t_l, the effect of the gas phase rate can generally be ignored. It is also important to realize, as we have shown, that a good estimate of k_g is accessible if t_g/t_l is varied,

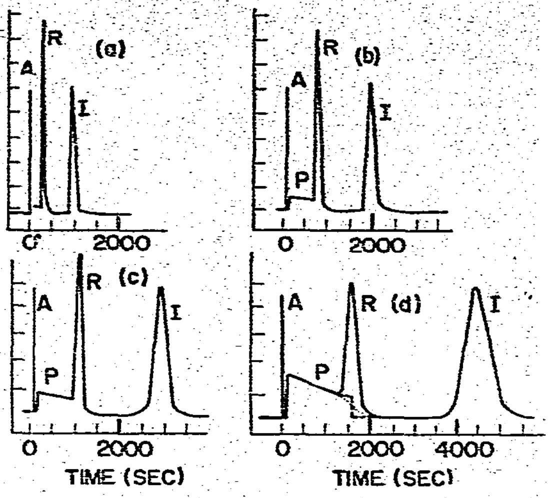

Fig. 4. Inert standard method for determining rate constants. Dimer III dissociating to form 2-methylcyclopentadiene at 180.08°. Column, 122 × 0.49 cm I.D., hexatriacontane–Gas Chrom Q (20:80). A = Air; P = product; R = reactant; I = inert phenyl ether. (a) 15% conversion; flow-rate, 65.7 ml/min (corr); $\Delta P = 31.3$ cm; (b) 25% conversion; flow-rate, 33.5 ml/min (corr); $\Delta P = 16.2$ cm; (c) 34% conversion; flow-rate, 22.05 ml/min (corr); $\Delta P = 10.6$ cm; (d) 50% conversion; flow-rate 15.6 ml/min (corr); $\Delta P = 6.8$ cm. In (d) the area under the dotted ramp line in the reactant peak approximates the area under the dashed line or product eluted with the reactant.

i.e., the percentage of liquid phase relative to solid support is varied for similar columns[1,2]. It is obtained from eqn. 8 and several values of k_{app} relative to t_g/t_l.

Product curve method[2,14,15]

The shape of a product curve on a reactor chromatogram as can be seen from Fig. 4d often resembles an exponential decay. The possibility that reaction rate con-

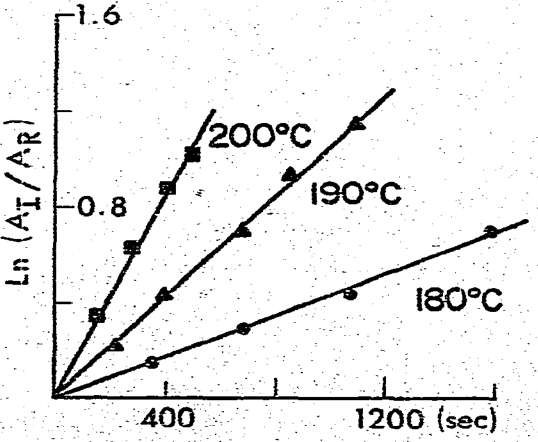

Fig. 5. First order rate plots of ln(inert area/reactant area) *vs.* liquid phase residence time for dimer III dissociation in hexatriacontane–Gas-Chrom Q. Points are averages of duplicate runs. Lines were adjusted to pass through the origin by subtracting the intercept (see eqn. 10) from each point.

stants may be obtained from the product curve then is strongly suggested if there is no reverse reaction. In fact an approach to obtaining a first order rate constant from the shape of the reactor product curve can be developed based on a material balance on the product in an "ideal" chromatographic reactor. The detailed development is shown in the Appendix. The result for a square wave input is

$$\text{Slope} = \left[\frac{\ln\,(\text{recorder response})}{\text{time}}\right] = -k'_{\text{app}} = \frac{-k_{\text{app}}\, t_{l,R}}{t_{l,R} - t_{l,P}} \tag{11}$$

where $t_{l,R}$ and $t_{l,P}$ are the residence times in the liquid phase of the reactant and the product, respectively. Both of these values can be obtained from chromatograms if t_g, the residence time in the gas phase, is also measured. It should be remembered that the chromatographic curve obtained for the product resembles that observed for frontal analysis of the same material[8]. Thus $t_{l,P}$ should be measured at one half the step height of the product curve.

RESULTS

Typical redrawn (for scale suitability) chromatograms obtained in this study for a range of conversions involving the dissociation of dimer III in hexatriacontane are shown in Fig. 4. Values of t_g and t_l were obtained by measuring from the time

TABLE I

LIQUID-PHASE RATE CONSTANTS, k_l, FOR DISSOCIATION OF METHYLCYCLOPENTADIENE DIMERS

Dimer	*Temp. (°C)*	*$k \times 10^3$ (sec^{-1})*				
		Silicone DC-550	*Poly(phenyl ether) (6-ring)*	*PDEAS**	*n-Hexatriacontane*	*Gas*
I	180	0.363±0.006**	0.502±0.005	0.496±0.016	0.345±0.009	—
	190	1.016±0.055	1.196±0.042	1.241±0.046	0.897±0.024	0.504±0.030
		(0.143)***	(0.136)	(0.456)	(0.091)	
	200	2.778±0.177	2.774±0.096	2.548±0.116	2.055±0.072	1.255±0.080
II	180	0.401±0.014	0.518±0.005	0.521±0.025	0.393±0.010	—
	190	1.185±0.032	1.269±0.040	1.413±0.055	0.964±0.015	0.485±0.026
		(0.126)	(0.121)	(0.408)	(0.084)	
	200	2.668±0.049	3.100±0.057	3.177±0.114	2.023±0.062	1.203±0.045
III	180	0.440±0.007	0.555±0.009	0.512±0.012	0.410±0.013	—
	190	1.185±0.024	1.391±0.015	1.244±0.037	1.023±0.033	0.605±0.034
		(0.109)	(0.099)	(0.326)	(0.069)	
	200	2.668±0.087	2.979±0.045	3.145±0.089	2.125±0.053	1.459±0.080
DCPD§	180	0.461±0.017	0.568±0.012	0.568±0.020	0.457±0.003	—
	190	1.189±0.04	1.280±0.01	1.393±0.04	1.077±0.01	0.601±0.034
		(0.127)	(0.165)	(0.401)	(0.115)	
	200	2.643±0.07	2.924±0.03	3.099±0.08	—	1.432±0.038

* Phenyldiethanolamine succinate.

** Standard deviation. Rate constants estimated by least squares analysis.

*** Values in parentheses are ratios of t_g to t_l measured at 190°.

§ Dicyclopentadiene (DCPD) constants reported in ref. 1.

TABLE II

ARRHENIUS PARAMETERS FOR DISSOCIATION REACTIONS IN VARIOUS SOLVENTS

Solvent	*Dimer I*		*Dimer II*		*Dimer III*		*DCPD*[*]	
	log_{10} A (sec^{-1})	*E_a (kcal/mole)*	*log_{10} A (sec^{-1})*	*E_a (kcal/mole)*	*log_{10}A (sec^{-1})*	*E_a (kcal/mole)*	*log_{10} A (sec^{-1})*	*E_a (kcal/mole)*
Silicone DC-550	—	—	15.1±0.4	38.4±0.9	15.2±0.8	38.4±1.8	14.6±0.1	37.2±0.2
Poly(phenyl ether) (6-ring)	14.3±0.5[**]	36.5±1.1[**]	15.1±0.2	38.2±0.4	14.0±0.7	35.8±1.6	13.3±0.3	34.3±0.7
PDEAS	13.5±0.9	34.9±2.0	14.2±0.1	36.1±0.2	15.3±0.5	35.9±1.0	14.2±0.4	36.1±0.9
n-Hexatriacontane	14.9±0.5	38.0±1.1	13.4±0.7	34.9±1.5	13.5±0.9	35.1±1.8	13.5±0.2	35.0±0.3
Gas	15.0±0.4	38.7±0.9	15.3±0.2	39.4±0.4	14.6±0.3	37.8±0.7	14.6±0.2	37.7±0.4

[*] Ref. 1.

[**] Standard deviation. Arrhenius parameters estimated by least squares analysis.

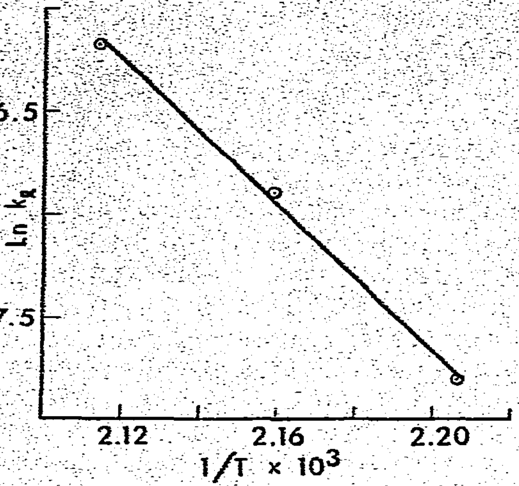

Fig. 6. Arrhenius plot for the data shown in Fig. 5, dimer III dissociation in hexatriacontane.

of pulse injection to the air peak (A), and from the time of emergence of the air peak to the reactant peak (R). Reactant areas were measured with a disc integrator, corrected for the presence of product with appropriate measurements[1,2,7].

Plots of the ln (inert area/reactant area) against residence time in the liquid phase are shown in Fig. 5 for dimer III in hexatriacontane on Gas-Chrom Q. For increased accuracy, two conversion runs are made at each flow-rate. The averages at several temperatures are shown in Fig. 5. The data give good linear plots for the temperatures shown; the other dimers give similar plots. The approach does seem quite satisfactory. The apparent rate constants obtained from these plots with eqn. 10 can then be converted to liquid phase rate constants with the aid of eqn. 8 and a knowledge of k_g. Values of k_g do not have to be known with great accuracy. Fortunately, they can be obtained by a gas chromatographic method with the use of eqn. 8. Such values, together with k_l values for our liquid phases and dimers, are listed in Table I. The measurements were not made exactly at the indicated temperatures. However, rate constants were adjusted slightly using an Arrhenius expression, so that reaction rates can be compared at a particular temperature.

A representative, computer-constructed Arrhenius plot for obtaining the energy of activation and pre-exponential factor is shown in Fig. 6, using the data of Fig. 5 for dimer III. With such plots, values for Arrhenius parameters in the solvents of interest can be obtained. Such parameters are listed in Table II together with values for the gas phase and dicyclopentadiene.

DISCUSSION

While we have only discussed relatively successful rate measurements, the limitations in deriving eqn. 4 should be remembered in applying it. The limitation at slow flow-rates is significant diffusion. However, very fast flow-rates cannot be employed either, since mass transfer processes can become important. The Van Deemter equation[16] applied without consideration of reaction can give some indication of upper flow limits (lower feasible conversions). Little effort was made to refine the data of Table I. However, it is apparent that the gas chromatographic method for obtaining kinetic data is viable for complex labile systems of the type studied here. For the complex methylcyclopentadiene dimers, only some kinetic data from Franklin's work on the dissociation of the liquid commercial mixture are comparable[4]. His values of 37.1 kcal/mole for the activation energy and 13.1 for the logarithm of A ($\sec^{-1}$) are quite compatible with our values for individual isomers in Table II.

On reviewing the data of Table I it can be seen that solvent effects are not great for the methylcyclopentadiene dimer dissociation[1]. However, these are large relative to substituent position effects[6]. Substituent effects can be significant; dimer I with its electron-donating methyl group close to the bridgehead does dissociate at a slower rate than do the other two dimers and the unsubstituted dicyclopentadiene. This is in agreement with other results on the retro Diels-Alder reaction when electron releasing groups tend to retard reaction[4,17] (or bond breaking). Dimer II tends to react at a slower rate than dimer III but does not always do so. The explanation for this is obscure. The effect of placement of methyl groups removed from the bridgehead carbon is quite small.

In Table I, the values of k_g, the rate constant in the gas phase, are most in doubt. For dicyclopentadiene, we have listed gas chromatographically determined gas phase rate constants from our laboratories which are about 75% of the values of Kwart *et al.*[18] and Herndon *et al.*[19]. The data of the latter two groups also show some variation. We are, of course, drawing fine comparisons in a region where small errors in Arrhenius parameters may cause considerable variation in absolute values. The interest in the value of the gas phase rate constant is strong because it is needed to calculate the value of the liquid phase rate constant according to eqn. 8. Our use of gas chromatographically determined values of k_g is based on the assumption that these are most pertinent to the experimental conditions[1,2]. Furtunately, the ratio of t_g/t_l generally is small, often of the order of 0.1 (see Table I). Thus the contribution of the accuracy of k_g to k_{app} on the determination of k_l is small and k_{app} generally approximates to k_l except in the case of phenyldiethanolamine succinate, where it is more significant, as indicated in Table I and by eqn. 8.

A comparison of the liquid phase rate constants for the methyl-substituted dimers with unsubstituted dicyclopentadiene also shows that the effect of the electron-donating substituent is to retard the rate[4,6]. As the substituent methyl group is removed further from the site of reaction, its effect is diminished, and rate constants for dissociation of dimers II and III differ from dicyclopentadiene at about only slightly more than experimental error.

The energies of activation and frequency factors for the reactions as shown in Table II often give a more detailed overview of reaction factors than rate constants alone. Unfortunately, experimental errors in the determination of such parameters often run high. It is well known that some error in the determination of one of these parameters can affect the derived value of the other. However, the weight of evidence here, combined with other evidence and the common view, indicates that solvents generally increase the rate of reaction[6,20], lowering both energy of activation and frequency factor. The latter is related to the entropy of activation, lower values reflecting more negative entropies of activation. Using the frequency factor criterion, solvent media generally do seem to have a "cage effect" less conducive to reaction than the less restricted gas phase condition.

Given the observed small solution effects, specific solution effects involving reactant–solvent interactions are difficult to identify. Of the solvents studied here, phenyldiethanolamine succinate and poly(phenyl ether) seem to promote reaction. For dimer III both solvents seem to lower the energy of activation.

The "inert standard" method is obviously best suited to laboratories with special chromatographs fitted for reproducible temperature control in both time and space. However, there are many situations where reactions take place in a chromatograph where it is desirable to measure or estimate rate constants from a single run during which time the temperature is constant. This consideration led us to investigate the "product curve" method further. With eqn. 11, it is possible to measure rate constants from a single run and compare them with the constants obtained by the inert standard method. An illustration of the appropriate plot is shown in Fig. 7. Agreement with the inert standard method is within about 20%, as indicated in the figure legend. We have made similar calculations and have found rate constants determined by this method generally to come within 20–30% of the rate constant. The parameters which govern the applicability of the method are still in the process of identification. However, high conversion and relatively low residence time in the gas phase, where product diffusion can take place, are factors which contribute to making the approach tractable. While this method requires further investigation, it does seem useful and adequately developed at this time. It adds to the information available from the product curve.

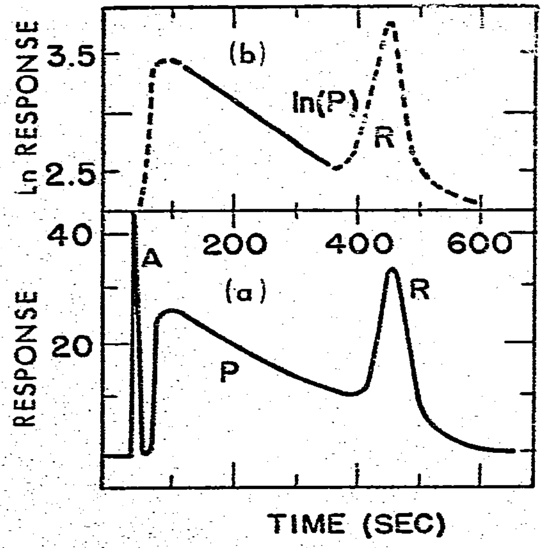

Fig. 7. Product curve method for determining rate constant illustrated by dimer III decomposition in a hexatriacontane–Gas-Chrom Q (20:80) column at 199.8°. Curve (a) shows product wave, P, decaying into reactant peak, R. Rate constant obtained by replotting P on logarithm scale as shown in (b) solid line. $k'_{app} = k_{app} \{t_{l,R}/(t_{l,R} - t_{l,P})\}$. This is for 68% conversion. k_{app} (product curve) = 0.00269 sec^{-1}; k_{app} (inert standard) = 0.00223 sec^{-1}; $t_{l,R}$ = 504 sec; $t_{l,P}$ = 40.8 sec.

Since vapor pressure data are not available for the dimers of this study, solution thermodynamic data for studying interactions cannot be obtained at this time. The present study does show the power of gas chromatographic techniques in that it is only through the application of preparative and analytical chromatography that pure samples for the kinetic investigation could be obtained. Furthermore, the GCR does prove to be a reasonably simple, useful, effective method for obtaining accurate kinetic data when its application is valid.

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APPENDIX

Product curve method[2,13–15]

The material balance for the product in a section of the GCR in the absence of diffusion is

$$f_g\left(\frac{\partial C_{g,P}}{\partial t}\right)+f_l\left(\frac{\partial C_{l,P}}{\partial t}\right)=-f_g\frac{\partial}{\partial x}\left[u(x)\,C_{g,P}\right]+f_g\,r_g+f_l\,r_l \qquad \text{(A1)}$$

where $C_{g,P}$ and $C_{l,P}$ are molar concentrations of product in the gas and liquid phases, respectively. Rates are for product formation. The initial and boundary conditions are:

$$C_{g,P}(x,0)=0;\; C_{g,P}(0,t)=0$$

For first order reaction, eqn. A1 can be rearranged to give

$$(f_g+K_Pf_l)\left(\frac{\partial C_{g,P}}{\partial t}\right)+f_g\frac{\partial}{\partial x}\left[u(x)\,C_{g,P}\right]=\eta_P\,(f_g\,k_g+f_l\,k_l\,K_R)\,C_{g,R} \qquad \text{(A2)}$$

if $K_P = C_{l,P}/C_{g,P}$, $K_R = C_{l,R}/C_{g,R}$ and η_P is number of moles of product formed from each mole of reactant.

Defining

$$\alpha_R = 1+\frac{f_l\,K_R}{f_g}$$

$$\alpha_P = 1+\frac{f_l\,K_P}{f_g} \qquad \text{(A3)}$$

$$\beta_1 = k_g+\frac{k_l f_l\,K_R}{f_g}$$

and substituting the appropriate expression for reactant concentration at the outlet[1,2] in the reactor

$$\alpha_P \left(\frac{\partial C_{g,P}}{\partial t}\right) + \frac{\partial}{\partial x}[u(x)\, C_{g,P}] = \frac{u(0)}{u(x)}\eta_P\, \beta_1\, \varphi\,[t - \alpha_R\, \tau(x)] \exp[-\beta_1\, \tau(x)] \tag{A4}$$

Defining transforms of $(C_{g,P})$ and $\varphi(t)$ by

$$\mathscr{L}\{C_{g,P}(x,t)\} = \overline{C_{g,P}}(x,s) = \overline{C_{g,P}},\ \mathscr{L}\{\varphi(t)\} = \varphi(s) \tag{A5}$$

With these definitions, the Laplace transform of eqn. A4 gives the differential equation

$$\alpha_P\, s\overline{C_{g,P}} + \frac{\mathrm{d}\,[u(x)\, \overline{C_{g,P}}]}{\mathrm{d}x} = \frac{u(0)}{u(x)}\eta_P\, \beta_1\, \varphi(s)\, \mathrm{e}^{-(\beta_1+\alpha_R\ s)\tau(x)} \tag{A6}$$

The equation is solved using the integrating factor

$$\exp\left[\alpha_P\, s \int \frac{\mathrm{d}x}{u(x)}\right] = \exp[\alpha_P\, s\tau(x)]$$

and the boundary condition

$$C_{g,P}(0,t) = 0$$

The result in the Laplace domain is

$$u(x)\, \overline{C_{g,P}} = \frac{u(0)\, \varphi(s)\, \eta_P\, \beta_1}{\beta_1 + (\alpha_R - \alpha_P)\, s}\,[\mathrm{e}^{-\alpha_P\ s\tau(x)} - \mathrm{e}^{-(\beta_1+\alpha_R s)\tau(x)}] \tag{A7}$$

The area under a product curve on a reactor chromatogram is

$$A_i = \int_0^t RR(\theta)\, \mathrm{d}\theta$$

where RR is the recorder response. The weight of sample eluted by time t from a column of length L is

$$W_i = a_g\, M_i \int_0^t u(L)\, C_{g,i}(L,\theta)\, \mathrm{d}\theta \tag{A8}$$

where a_g is the cross section area of the gas phase and M_i is the solute molecular weight. Area and weight are related by

$$S_i\, \mathrm{d}A_i = \mathrm{d}W_i \tag{A9}$$

where S_i is the sensitivity factor for component i.

Combining these three equations

$$RR(t) = \frac{a_g M_i}{S_l} u(L) C_{g,i}(L,t) \tag{A10}$$

also

$$\alpha_R = \frac{(t_g + t_{l,R})}{t_g} = \frac{t_R}{t_g} \tag{A11}$$

$$\begin{aligned} \alpha_P &= \frac{(t_g + t_{l,P})}{t_g} = \frac{t_P}{t_g} \\ \beta_1 &= \frac{k_{\mathrm{app}}\, t_{l,R}}{t_g} \end{aligned} \tag{A12}$$

where $t_{l,P}$ and $t_{l,R}$ are residence time of product and reactant in the liquid phase

$$RR(t) = \frac{u(0)\, a_g M_P}{S_P} \frac{\eta_P \beta_1}{\alpha_R - \alpha_P} \mathscr{L}^{-1} \left\{ \frac{\varphi(s)}{s + \dfrac{\beta_1}{\alpha_R - \alpha_P}} [\mathrm{e}^{-s\alpha_P t_g} - \mathrm{e}^{-(\beta_1 + s\alpha_R)t_g}] \right\} \tag{A13}$$

Since $\varphi(s)$ appears in eqn. A13, the product curve depends on the input wave form. It is useful to define a new apparent rate constant

$$k'_{\mathrm{app}} = \frac{\beta_1}{\alpha_R - \alpha_P}$$

leading to

$$k'_{\mathrm{app}} = \frac{k_{\mathrm{app}}\, t_{l,R}}{t_{l,R} - t_{l,P}} \tag{A14}$$

Also defining

$$B_0 = u(0) \frac{a_g M_R \eta_P \beta_1}{(\alpha_R - \alpha_P) S_P} \tag{A15}$$

eqn. A13 becomes

$$RR(t) = B_0 \mathscr{L}^{-1} \left\{ \frac{\varphi(s)}{s + k'_{\mathrm{app}}} [\mathrm{e}^{-st_P} - \mathrm{e}^{-st_R - k'_{\mathrm{app}}(t_R - t_P)}] \right\} \tag{A16}$$

Applying the convolution and shifting theorems to eqn. A16 and solving for the recorder response to product eluted between t_P and t_R (product retained less than reactant)

$$RR(t) = B_0\, \mathrm{e}^{-k'_{\mathrm{app}}(t - t_P)} \int_0^{t - t_P} \varphi(v)\, \mathrm{e}^{k'_{\mathrm{app}} v}\, \mathrm{d}v \tag{A17}$$

A unit square wave input is defined as

$$\varphi(t,t_0) = \begin{cases} 1/t_0 & t < t_0 \\ 0 & t > t_0 \end{cases}$$

for an input of $B_0\,\varphi(t,t_0)$. Eqn. A17 becomes

$$RR\,(t) = (B_0\,C_0/k'_{\mathrm{app}}\,t_0)\,[\mathrm{e}^{k'_{\mathrm{app}}t_0} - 1]\,\mathrm{e}^{-k'_{\mathrm{app}}(t-t_p)} \tag{A18}$$

for $t_P + t_0 < t < t_R$.

From the logarithm of this equation, a plot of ln recorder response *versus* time has a slope of $-k'_{\mathrm{app}}$.

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