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FRONTAL ANALYSIS OF PRODUCT PEAKS FROM GAS CHROMATOGRAPHIC REACTORS

DICYCLOPENTADIENE AND DI-*tert.*-BUTYL PEROXIDE DECOMPOSITION

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SUMMARY

The chromatographic curve resulting from pulse injection of a reactant into a chromatographic column may contain significant information about products. Under some conditions, the elution volume or time at one-half the step height of the product curve approximates the characteristic elution volume, or time, of product material. This may even be true when reactants give several products. Such information may be used for product identification and obtaining solution thermodynamic data.

INTRODUCTION

In earlier studies on the use of the gas chromatographic column as a chemical reactor, we have shown how chromatograms can be used to study the kinetics of dissociation reactions¹⁻³ and how some of these chromatograms can be used to obtain substantial information about column homogeneity and packing^{2,4,5}. Here, we describe additional information about reaction products available from product curves on reactor chromatograms, including aids to identification. The unimolecular kinetic systems chosen for study were the well known dicyclopentadiene dissociation and the somewhat more complex di-*tert.*-butyl peroxide decomposition.

A typical reaction chromatogram for the formation of cyclopentadiene from dicyclopentadiene is shown in Fig. 1a. The portion of the chromatogram due to formation of cyclopentadiene closely resembles the chromatogram obtained in frontal analysis, *i.e.* when the column feed is changed from pure carrier gas to carrier gas containing a solute vapor at constant concentration. Since the characteristic retention volumes of chromatographic peaks in frontal development with partition chromato-

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graphy occur at one-half the step height^{6,7}, it seemed worthwhile to investigate the corresponding portions of elution curves of reaction products from the chromatographic reactor^{2,8}.

EXPERIMENTAL

The constant-temperature apparatus described earlier¹ was used. Columns were 0.63 cm O.D. stainless steel or PTFE-lined aluminum. Recorders were run at relatively high speeds of up to 12 in./min to facilitate time measurements on product rise curves. Small "blips" were placed automatically on chromatograms at 5- or 10-sec intervals to aid in timing. An illustrative chromatogram on which $t_{\frac{1}{2}}$ measurements (time at $\frac{1}{2}$ step height) were made is shown in Fig. 1b.

Reactant pulses of 0.4 to 0.7 μ l were used. Characteristic retention times of cyclopentadiene, acetone, *tert.*-butanol and other reaction products were obtained by separate injections of small pulses of pure materials. Air retention time was measured separately where necessary. Trapped materials for study of butyl peroxide decomposition were collected in a glass U-tube attached at the outlet of column D and immersed in dry ice-acetone. A drop of chlorobenzene was placed in U-tubes to aid trapping. Collected products were analyzed on analytical columns of hexatriacontane (15%) and on D.C. Silicone 550 columns (15%).

Chromatographic reactor columns were: (A) 15% Hexatriacontane-Gas-Chrom Q, stainless steel, 12 ft. (B) 25% Hexatriacontane-Gas-Chrom Q, stainless steel, 12 ft. (C) 30% Hexatriacontane-Gas-Chrom Q, PTFE-lined aluminum, 5 ft. (D) 30% Dow Corning Silicone 200 (D.C. 200) (350 cS)-Gas-Chrom Q, PTFE-lined aluminum, 6 ft. Gas-Chrom Q (Applied Science Labs., State College, Pa., U.S.A.) was 60-80 mesh.

RESULTS AND DISCUSSION

In frontal analysis^{6,7}, assuming (1) a linear isotherm along the column, (2) negligible diffusion contributions, (3) rapid equilibration (mass transfer) between phases relative to flow-rate, and (4) a column of uniform composition, then

$$c/c_0 = \frac{1}{2}$$

at the characteristic retention time or retention volume from the time of introduction of a solute in a chromatographic column, where c_0 is the concentration of solute in the feed at the column inlet and c is the observed concentration of solute in the carrier gas at the column outlet. The concentration at the outlet eventually becomes c_0 . From Fig. 1a and a knowledge of kinetic phenomena, we might consider the initial formation of a product in carrier gas from a reacting pulse at the column inlet to approximate the introduction of carrier gas with a constant equivalent concentration of product compound. This would be especially true for situations in which the proportion of reactant sample reacting per unit time is relatively small (during passage through the column) so that the slope of the product curve in the chromatogram is small.

Some representative results for the dicyclopentadiene \rightarrow cyclopentadiene

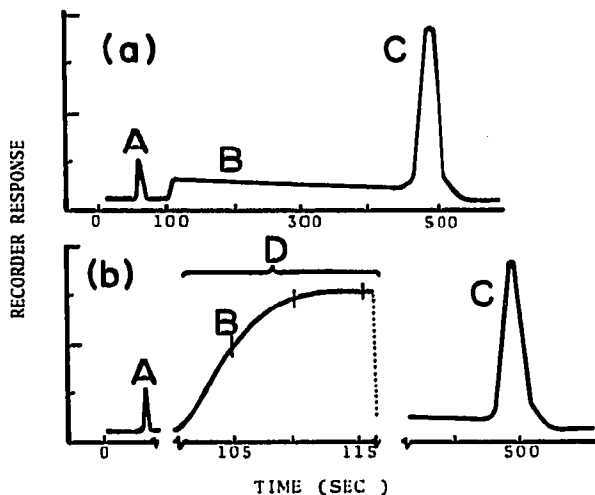


Fig. 1. (a) Typical reaction chromatogram for dicyclopentadiene dissociation at 190° (Table I, Run A-3) on Hexatriacontane-Gas-Chrom Q (15:85). Flow-rate, 87.3 ml/min of helium through 12-ft. stainless-steel column. A = Air peak; B = cyclopentadiene product; C = dicyclopentadiene reactant. (b) Similar to (a). D = Recorder speed increased over this time range, attenuation decreased to allow enlargement of leading edge of product curve B and measurement of $t_{1/2}$.

system are presented in Table I. The average ratio of $t_{1/2}$, the time at which the product elution front reaches one half of its maximum value, to the time of elution of a pulse of product is 1.016 ± 0.024 for reasonable column flow-rates. At faster flow-rates with heavily loaded columns the approximation to unity is less valid; this can be attributed to a slow mass transfer which limits equilibration between phases (see assumption (3) above). This is especially evident in the B series on a column with 25% liquid phase. Deviations above unity are consistent with mass transfer from the liquid phase limiting equilibration. However, even for this series the ratio of $t_{1/2}$ to t_{CPD} is remarkably close to unity. On the lower loaded column of the A series, the relationship holds even for faster flow-rates. Errors and deviations are probably due to experimental error over the small time spans with which we are concerned here; this can be noted in the sample chromatogram curve (b) of Fig. 1 on which a $t_{1/2}$ measurement was made.

A significant feature of our observation is the conclusion that reliable retention volumes can be obtained for products from reactor chromatograms under proper conditions. Thus, reaction products can be identified through comparison with retention volumes of known materials. Furthermore, if retention data are required for troublesome or unstable materials, the need for separate preparation is eliminated if these materials are the product of the reaction under investigation.

Similar supporting results for the validity of the $t_{1/2}/t_{Product}$ relationship were obtained in a di-*tert.*-butyl peroxide decomposition study in hexatriacontane, as shown in Tables II and III. Di-*tert.*-butyl peroxide is known to decompose to form acetone or *tert.*-butanol as well as methane and ethane⁹⁻¹¹. Reactor chromatograms obtained for this decomposition are shown in Fig. 2. At an optimum flow-rate, acetone and *tert.*-butanol could be separated sufficiently for determination of a half

TABLE I

DICYCLOPENTADIENE DISSOCIATION —PRODUCT ELUTION STUDY

CPD = Cyclopentadiene.

Run*	$t_{\frac{1}{2}}$ ^{**} t_{CPD}	CPD elution time (sec) ^{**}	Conversion (%)	Flow-rate (ml/min) ^{***}	Column temperature (°C)
B-1	0.990	131.7	97.5	34.8	190
B-3	1.050	66.6	65	83.7	—
B-5	1.065	46.5	49.7	155.9	—
Av.	1.035 ± 0.040				
A-2	1.005	57.1	59.2	39.6	190
A-3	1.020	32.6	40.9	87.3	—
A-5	1.035	24.3	32.2	137.3	—
A-6	1.008	24.4	32.2	136.9	—
Av.	1.0117 ± 0.014				
A-1	1.010	98.1	51.2	21.3	180
A-2	1.008	61.5	36.2	40.6	—
A-3	0.995	38.1	24.0	83.4	—
A-4	0.994	33.0	21.1	103.6	—
Av.	1.002 ± 0.008				
All	1.016 ± 0.0024				

* Indicates column (see Experimental) and illustrative run.

** Measured from air elution time.

*** At column temperature and column outlet pressure.

peak time for each as shown in the enlarged curve (b) of Fig. 2. The $t_{\frac{1}{2}}/t_{\text{Product}}$ ratios are quite close to unity for both acetone and *tert.*-butanol (Tables II and III). The agreement is impressive considering no special high-speed equipment was used so that a fraction of a second in peak measurement would result in a several per cent

TABLE II

DI-*tert.*-BUTYL PEROXIDE DECOMPOSITION

Column temperature, 180°.

Run*	$t_{\frac{1}{2}}$ (B) ^{**} t_{Acetone}	$t_{\frac{1}{2}}$ (C) ^{**} $t_{\text{tert.-Butanol}}$	Acetone elution time (sec)	<i>tert.</i> -Butanol elution time (sec)	Conversion (%)	Flow-rate (ml/min) ^{***}
C-1	1.018	1.035	10.9	14.5	21.4	91.4
C-2	1.056	1.079	10.8	14.45	21.5	91.2
C-3	1.009	1.036	11.05	14.90	21.5	91.2
C-5	0.967	0.990	12.3	17.2	23.7	77.0
C-6	0.976	0.971	12.6	17.8	24.1	75.9
Av.	1.005 ± 0.036	1.022 ± 0.043				

* Indicates column used (see Experimental) and illustrative run.

** Measured from air elution time for peaks B and C of Fig. 2, as indicated.

*** At column temperature and column outlet pressure.

TABLE III
RETENTION VOLUMES RELATIVE TO DI-*tert.*-BUTYL PEROXIDE
DBP = Di-*tert.*-butyl peroxide.

Run	$t_{\frac{1}{2}}(B)^*$	t_{Acetone}	$t_{\frac{1}{2}}(C)^*$	$t_{\text{tert.-Butanol}}$
	t_{DBP}	t_{DBP}	t_{DBP}	t_{DBP}
C-1	0.219	0.215	0.296	0.287
C-2	0.224	0.212	0.306	0.283
C-3	0.220	0.218	0.305	0.294
C-5	0.208	0.215	0.298	0.301
C-6	0.211	0.216	0.288	0.295
Av.	0.216 ± 0.007	0.215 ± 0.002	0.299 ± 0.007	0.292 ± 0.007

* Measured from air elution time for peaks B and C of Fig. 2, as indicated.

error in the ratio. Some improvement in the ratio of $t_{\frac{1}{2}}$ to product elution times could be observed by using relative retention times (di-*tert.*-butyl peroxide reference) as shown in Table III. The results for *tert.*-butanol are further complicated by the fact that an extrapolation of a new baseline (line XY in Fig. 2b) was necessary for evaluating the one-half peak height time. Hence, when parallel reactions occur in a column and when adequate separation of frontal elution curves occurs as in Fig. 2a, it is possible to facilitate product identification by comparing elution times of the frontal section of elution curves with elution times of pulses of known materials obtained by conventional means.

When the di-*tert.*-butyl peroxide decomposition reaction was studied in D.C. 200, more ambiguous results were obtained. Separate resolved curves corre-

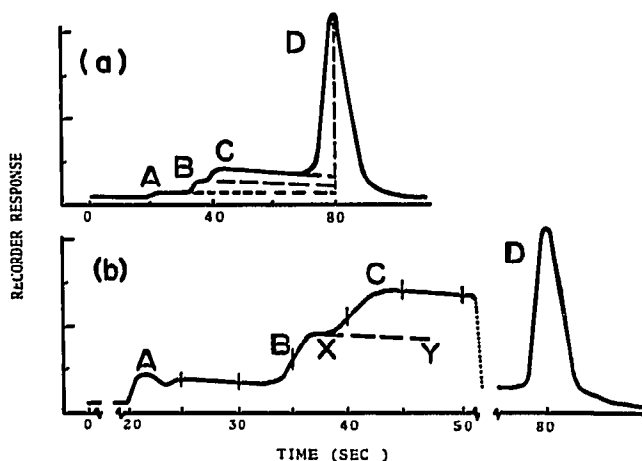


Fig. 2. (a) Typical reaction chromatogram for di-*tert.*-butyl peroxide decomposition at 180° (Tables II and III, Run C-3). Flow-rate, 77.0 ml/min of helium through 5-ft. PTFE-lined aluminum column. A = Air, methane and ethane; B = acetone product; C = *tert.*-butanol product; D = di-*tert.*-butyl peroxide reactant. (b) Similar to (a). Expanded portion of chromatogram from increasing recorder speed and decreasing attenuation. Line XY is corrected extrapolated baseline to assist $t_{\frac{1}{2}}$ measurement for C.

sponding to acetone and *tert.*-butanol could not be obtained since the difference between their retention times was less in this phase than found with hexatriacontane.

In a series of preparative runs at 180° and a flow-rate at the column outlet of 26.0 ml/min, $t_{\frac{1}{2}}$ (42.3 sec) was found to be closer to acetone (41.2 sec) than *tert.*-butanol (48.0 sec). Di-*tert.*-butyl peroxide had a total residence time of 201.6 sec, including the gas phase residence time of 62.0 sec. When product was collected and analyzed on a hexatriacontane column, with the assumption that areas are proportional to weight in the outlet carrier gas and correcting for molecular weight, in the outlet carrier gas, acetone was found to predominate by an estimated ratio of about 6 to 1. A considerably smaller amount of unidentified product, possibly isobutylene oxide, was also noted in the chromatogram. The unseparated collected product has an elution time within 1.8% of the observed product $t_{\frac{1}{2}}$ time when reinjected into the D.C. 200 column as a pulse. While the trapping experiments were not particularly accurate, they demonstrated that the product chromatogram gave clues to the product ratio in di-*tert.*-butyl peroxide decomposition from the position of the half peak relative to the elution time of the pure products.

It is to be remembered that the time necessary for an inert or air peak to emerge would indicate sample residence time in the gas phase and time measured from the air peak to emergence of a reacting substance would indicate reactant time in the stationary phase¹². The qualitative product distribution from the chromatographic reactor run in D.C. 200 would reflect the fact that *tert.*-butyl peroxy radicals were formed both in the gas phase, where they tend to produce acetone, and in the D.C. 200 poly(dimethylsiloxane) phase, from where abstraction of hydrogen from a methyl group is known to be difficult¹³. The product distribution indicated by Fig. 2a for reaction in hexatriacontane shows a considerably greater proportion of *tert.*-butanol. Abstraction of a hydrogen atom for formation of this product is known to be considerably easier¹³ from the numerous methylene groups (secondary hydrogen) of hexatriacontane. The possibility of studying facets of the peroxide radical and similar decompositions is evident. Additional discussion is deferred for the present since the di-*tert.*-butyl peroxide decomposition is under further investigation in our laboratory.

It is difficult to obtain data from frontal analysis of product fronts where high conversion takes place early in the column since the emerging products give signals more closely resembling conventional peaks from gas-liquid partition chromatography. Low constant conversion through the column more nearly resembles the frontal development situation.

To date, we have not tested our reacting systems where a considerable amount of adsorption is involved and no conclusions can be drawn regarding these systems at this time.

The results of the experiments that we describe here make it apparent that the product wave obtained from the chromatographic reactor can give useful information to help identify products of reaction. From retention volumes measured from the half peak position of the product curve, one can calculate solution thermodynamic data, such as activity coefficients, heats of solution, etc., for reactive or unstable materials in the liquid packing of the chromatographic column since retention volumes can be related to these quantities^{1,14}.

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