

at room temperature so that the titrant was added over a period of 13 to 14 minutes, the normality of the cobalt(III) was $7.100 \times 10^{-3} \pm 2$ parts per thousand. The 1% difference in these two sets of titrations must be attributed to the increase of the reaction of cobalt(III) with water in the rapid titrations because of the high local concentration of titrant. If, on the other hand, this titration was performed rapidly at 0° C., a larger volume of titrant than used at room temperature was required, and the normality of the cobalt(III) was calculated to be 6.798×10^{-3} . These results at 0° C. suggest that even more cobalt(III)

must be consumed in oxidizing water than in those titrations carried out at room temperature. This explanation would appear to be valid only if the rate of the reaction between cobalt(III) and water decreases less rapidly with temperature than does the reaction between iron(II) and cobalt(III). A study of the rates of various oxidation-reduction reactions as a function of temperature is now under investigation.

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Study of Organic Structure via Mercury-Sensitized Photolysis and Gas Chromatography

Alcohols and Esters

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► The controlled, mercury-photosensitized, liquid phase photolysis of some simple aliphatic alcohols and straight chain esters has been studied and the products have been analyzed by gas-liquid chromatography. Each of the compounds studied yields a characteristic degradation pattern suitable for "fingerprint" identification of special structural features within the molecule. Within any of the series studied, the major mechanism of degradation is independent of chain length, which enables the positive identification of the irradiated structure through the formation of homologous or common products. Numerical constants involving the retention of these photolytic decomposition products using a linear programmed temperature gas chromatographic column have been tabulated, and these constants are characteristic of chain branching and the functional groups present in the irradiated material. The expression of retention data as retention indices allows the reproduction of these data in other laboratories.

The combination of pyrolysis and gas-liquid chromatography (GLC) has often been recommended for qualitative identification of materials as well as for extending GLC to the analysis of compounds of low volatility. Perry (12) has given a thorough review of the tech-

niques and potentialities of pyrolysis-GLC.

Unfortunately, the nature and relative amounts of pyrolysis products vary greatly with the experimental conditions and apparatus used (2). The maximum temperature of the filament or pyrolysis chamber, the rate of heating, the sample size, the prior history of the filament or pyrolysis chamber and its composition all appear to influence the results. Thus, data obtained are difficult to reproduce from laboratory to laboratory. The effect of pyrolysis temperature on the amount and identity of the products formed is particularly striking and has been studied by several workers (2, 4, 11). Janak (3) found that rearrangements often occur in the pyrolysis of barbituric acid derivatives, leading to unexpected products. Keulemans and Perry (4) showed that rearrangement and secondary reactions are dependent upon sample size as well as pyrolysis temperature.

Most of the recent work in this area has been concerned primarily with the development of experimental techniques for improving the reproducibility of pyrolysis. Pyrolysis-GLC has remained predominantly a technique in which identification depends upon the possession of previously obtained pyrolysis patterns with which the pattern of interest may be compared through careful control of all experi-

mental parameters. Very little progress has been made concerning the basic modes of degradation which would allow this technique to be used as a means of qualitative structural determination for compounds previously unstudied.

It is the purpose of this work to investigate the use of high-intensity monochromatic mercury resonance radiation for the controlled degradation of organic compounds, with subsequent analysis of the products by GLC. Ultraviolet radiation appears to have certain advantages which enhance its use as a degradative means for identification and structural determinations. The apparatus used in photolytic studies is relatively inexpensive and can be easily standardized. The conditions of degradation may be carefully controlled and accurately known. The product yields may be maintained at very low values (< 2%), thus minimizing secondary reactions and changes in matrix. The number of products expected from degradations by mercury resonance radiation is much less than in the case of techniques such as pyrolysis in which the samples are subjected to more severe energetic conditions. The breakdown patterns are thus more simple and easy to interpret.

In order for a compound to undergo photolytic reaction it must absorb the

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incident radiation. Many compounds do not absorb sufficient amounts of mercury resonance radiation for direct decomposition. However, when mercury resonance radiation is employed, metallic mercury may be used as a photosensitizer. A photosensitizer will absorb resonance radiation and will impart this energy to other molecules not absorbing the radiation directly. Thus, photolytic degradation may be extended to essentially all organic compounds.

The studies reported in this paper were carried out in the liquid state. Pibbs and Darwent (13) and Kuntz and Mains (9) have previously shown that paraffinic hydrocarbons also undergo mercury-sensitized photolysis in the liquid state. Liquid phase irradiations are conveniently performed owing to the relative ease of sample handling, fewer sample volatility requirements, and negligible pressure dependence. For this technique to be successful it is necessary that mercury be soluble enough in the compound under investigation to absorb significant quantities of incident resonance radiation during a reasonable period of irradiation. Kuntz and Mains (10) summarized the solubility of mercury in some typical organic compounds. In all cases the mercury solubility was shown to lie in the micromolar range, an amount sufficient for mercury-sensitized reactions to take place.

To show the usefulness of the technique for compounds absorbing very little or none of the mercury resonance radiation, a systematic study was made concerning the degradation behavior of some simple aliphatic alcohols and aliphatic esters.

EXPERIMENTAL

Chemicals. Merck anhydrous methanol (acetone-free) was used without further purification as were absolute ethanol (U.S.I.) and isopropanol (Mallinckrodt). *t*-Butyl alcohol was distilled from sodium. The other alcohols and esters were purified by GLC using conventional collection devices which allowed the trapped pure compound of interest to be centrifuged to the tip where saturation with a droplet of mercury could take place. Each of the compounds irradiated was previously checked to assure chromatographic purity. In a few cases small amounts of impurity (<0.5%) were tolerated.

Apparatus. A high-intensity, custom-built helical mercury resonance source (Type SC-2537, Order No. Z-1500-097, Englehard Hanovia, Inc., Newark, N. J.) was used in this study. The lamp was operated in a circuit of conventional design. Under the conditions of operation the lamp emits 97% of its ultraviolet output as the 2537 Å resonance line of mercury, with ap-

proximately 2% being emitted at 1849 Å. The lamp was operated in a hood using a gentle exhaust to prevent absorption of radiation by generated ozone.

The irradiation compartment consisted of a 5-mm. a.d. vertical quartz tube surrounded by a quartz water jacket maintained at $25^\circ \pm 0.5^\circ$ C. by circulated distilled water. The lamp and compartment were arranged such that their axes were coincidental. A glass rod was inserted into the 5-mm. quartz tube from the bottom to support the samples contained in sealed quartz capillaries for irradiation. Aluminum foil was placed around the resonance lamp to maximize radiation reaching the sample by reflection.

Both a Micro-Tek GC 2500R and a Micro-Tek DSS 172 DPFF gas chromatograph with dual flame ionization detectors and linear programmed temperature operation were used during the course of this work. A temperature program rate of 5.7° C./minute and a helium flow rate of 42.2 ml./minute were used to obtain product retention data.

Two 7-foot, $\frac{1}{4}$ -inch Carbowax 20M columns were used in these studies. The two columns consisted of 15% by weight of liquid phase coated on 80/100-mesh acid-washed Chromosorb W and 60/80-mesh hexamethyldisilazane-treated Chromosorb P (Johns-Manville), respectively. These columns were conditioned before use for 48 hours at 200° C. with a helium flow rate of 40–45 ml./minute. The weight of liquid phase in the two columns was 1.979 and 2.739 grams, respectively. The use of the polar Carbowax 20M column causes the rapid elution of hydrocarbons. In some cases high molecular weight hydrocarbons may then be eluted conveniently, although their molecular weight is much higher than the parent compound.

The irradiated samples were introduced to the gas chromatograph using an F and M Model SI-4-2A solid sampler (F and M Scientific Corp., Avondale, Pa.), which permitted the quartz irradiation capillary to be broken in the injection port and its contents swept into the column without loss. The injection port of the DSS 172 DPFF was enlarged to accept the sampler.

The injection port temperature was generally maintained in the range 160° – 210° C. in these studies, so that the temperature was always at least 15° C. above the boiling point of the compound being studied. Too high an injection port temperature is undesirable, since possible decomposition of the sample on hot quartz may occur. In working with the tertiary alcohols, it was necessary to reduce the injection port temperature to the range 80° – 110° C. to prevent noticeable thermal decomposition.

Procedure. The samples to be irradiated were saturated with triply-distilled mercury which had been filtered to remove dust and oxide. Saturation was accomplished by agitation at room temperature for 20

minutes or by insertion of a small droplet of mercury into the collection device used to trap the chromatographically-purified sample. A small amount of the mercury-saturated sample was transferred with a microsyringe to a weighed 1-mm. thin-walled quartz capillary tubing sealed at one end. The liquid sample was forced into the sealed end of the capillary by agitation or centrifugation, and the unsealed end of the sample capillary was attached to a vacuum line where the sample was degassed by two freeze-thaw cycles. During the freeze cycles, the headspace above the sample was heated with heating tape to freeze-dry minute amounts of liquid to the bulk sample. The headspace was also swept with helium during the thaw cycles to replace air in the capillary. After degassing, the capillary was sealed with a H_2 - O_2 torch while the sample was frozen and attached to the vacuum line to prevent entrance of oxygen or moisture. For an indication of the effect of sample size the weight of the sample was determined by difference. The sealing procedure reduces thermal decomposition of the sample to a negligible amount, and the entire operation requires only 5–10 minutes. The vapor portion of the sealed sample was wrapped with opaque tape prior to irradiation to minimize vapor phase photolysis. The sample was then inserted (liquid end down) into the irradiation compartment.

The irradiated samples were injected for chromatographic analysis after allowing the flow system to re-equilibrate after the insertion of the sampler and capillary into the injection port. This procedure also allowed the contents of the capillary to vaporize for rapid subsequent transfer to the column.

Peak areas were measured with a Keuffel and Esser compensating polar planimeter, reproducible to ± 0.1 cm.²

RESULTS AND DISCUSSION

Qualitative Observations of Photolytic Degradation Patterns. ALCOHOLS. The straight-chain primary aliphatic alcohols C_1 – C_6 , methyl secondary aliphatic alcohols C_3 – C_5 and C_8 , and tertiary aliphatic alcohols C_4 and C_5 were systematically irradiated and chromatographed. Figures 1–3 show the chromatographic "spectra" of these irradiated alcohols. The exact retention position of the parent compound was determined in an independent measurement using a small sample under identical chromatographic conditions.

The irradiation of each alcohol results in a distinct chromatogram suitable for "fingerprint" identification, each "spectrum" being unique for a given alcohol. These qualitative differences are even more remarkable when comparing data among the three homologous series. Of particular interest is the ability to distinguish among isomeric alcohols.

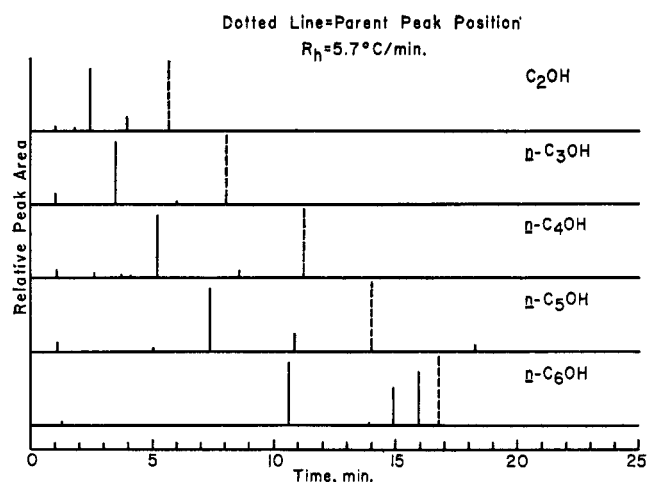


Figure 1. Chromatographic "spectra" of primary alcohols C_2-C_6 . Irradiated 10 min.; Carbowax 20M; flow rate 42.2 ml./min.; initial temp. 60°C .

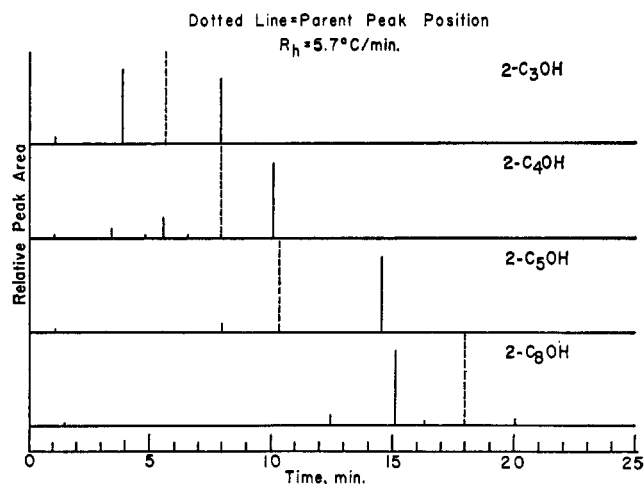


Figure 2. Chromatographic "spectra" of methyl secondary alcohols C_3-C_6 and C_8 . Irradiated 3 min.; Carbowax 20M; flow rate 42.2 ml./min.; initial temp. 60°C .

In addition, unsaturation influences the irradiation products of an alcohol where the two alcohols, *n*-propanol and allyl alcohol, were found to be readily distinguished. Chain branching greatly influences the products obtained where no difficulty was found in distinguishing *n*-butanol and *i*-butyl alcohol. *n*-Hexanol and cyclohexanol, aliphatic and alicyclic C_6 -alcohols, may also be distinguished by their irradiation products.

ESTERS. The following straight-chain aliphatic esters were irradiated for 3 minutes and chromatographed: ethyl esters (C_4-C_6 , C_8-C_9), methyl esters (C_3-C_5 , C_7), acetates (C_3-C_6 , C_8-C_9), and formates (C_4-C_7). Figures 4-7 show chromatographic "spectra" of these irradiated esters. The retention positions of the parent compounds were determined independently using small samples under identical chromatographic conditions. Each ester yields a

characteristic photolysis chromatogram suitable for "fingerprint" identification. The differences in degradation behavior are even more remarkable when comparing more than one type of ester, especially isomeric esters of different types.

Quantitative Trends and Correlations. **ALCOHOLS.** A summary of product data for the alcohols studied is shown in Table I. The peak positions are given as programmed temperature retention indices (14), and the peak areas are shown normalized to the major product peak area. These data show that each alcohol in a given homologous series systematically yields several products, each of which is a member of a homologous series. Therefore each homologous product appears on the chromatogram separated from the parent alcohol by a number of retention index units, $\Delta I = I_{\text{parent}} - I_{\text{product}}$, inde-

pendent of chain length within a series irradiated. Such spacings (ΔI) are thus characteristic of a particular group of alcohols and identify the structure of the alcohol moiety—i.e., primary, secondary, or tertiary. In addition, some of the alcohols studied yield distinctive product peaks which serve to distinguish them more qualitatively from their homologous neighbors. The irradiation chromatogram of methanol, however, is quite distinct and does not conform to the trend previously described.

The major product of each primary alcohol is the corresponding aldehyde, *B*, while a light hydrocarbon, *A*, as well as another product homologue, *C*, are also formed. The amount of hydrocarbon formed in each case is quite small compared to the aldehyde yield.

Secondary alcohols yield the corresponding ketone, *B*, as an important product, while also yielding a light

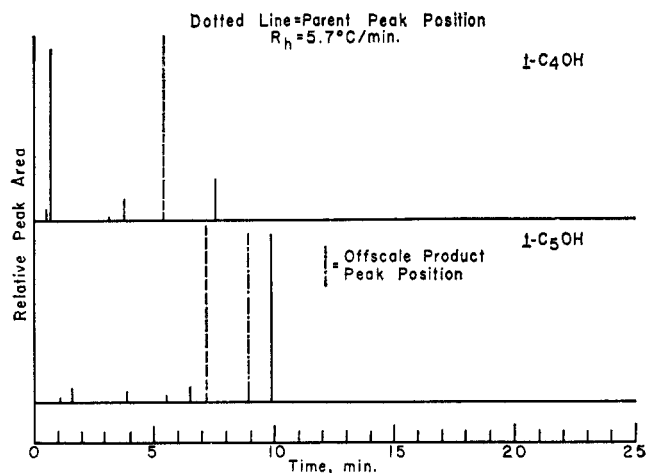


Figure 3. Chromatographic "spectra" of tertiary alcohols C_4 and C_5 . Irradiated 4 min.; Carbowax 20M; flow rate 42.2 ml./min.; initial temp. 60°C .

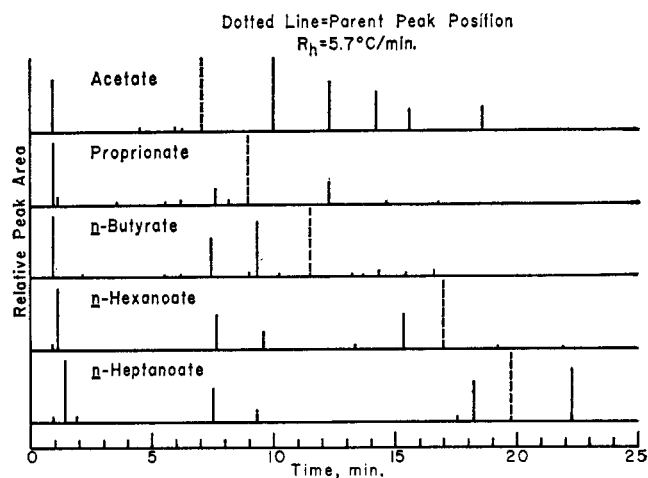


Figure 4. Chromatographic "spectra" of ethyl esters C_4-C_6 and C_8-C_9 . Irradiated 3 min.; Carbowax 20M; flow rate 42.2 ml./min.; initial temp. 60°C .

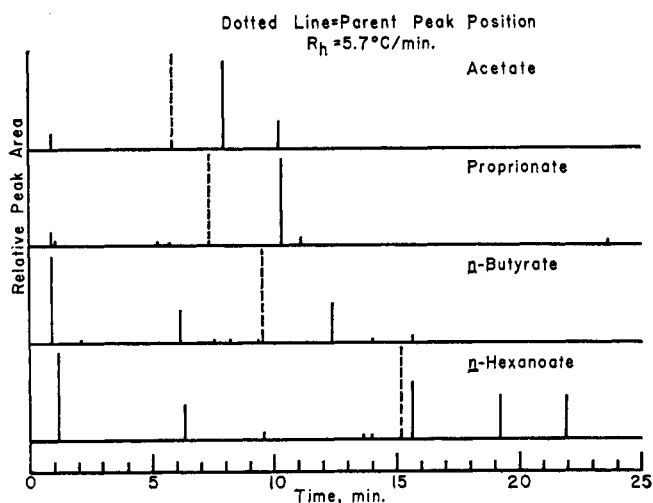


Figure 5. Chromatographic "spectra" of methyl esters C_3 – C_7 and C_9 .

Irradiated 3 min.; Carbowax 20M; flow rate 42.2 ml./min.; initial temp. 60° C.

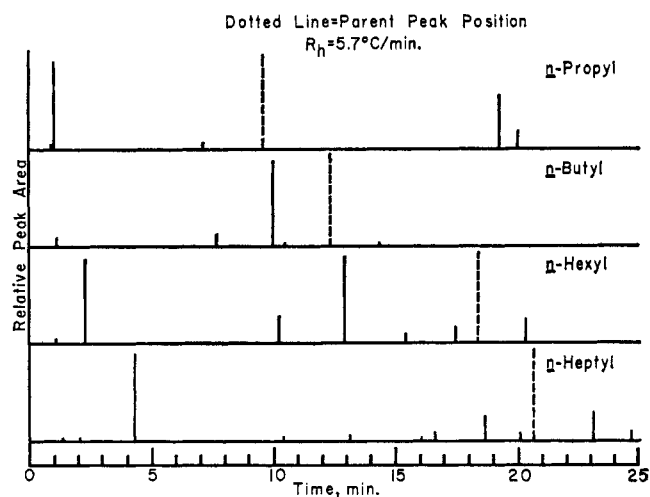


Figure 6. Chromatographic "spectra" of acetates C_3 – C_7 and C_9 – C_{13} .

Irradiated 3 min.; Carbowax 20M; flow rate 42.2 ml./min.; initial temp. 60° C.

hydrocarbon, *A*, and another product homologue, *C*. The amount of hydrocarbon formed relative to the ketone is invariant (within experimental error) through the series, while the yield of product *C* exceeds that of the ketone only for 2-butanol and 2-pentanol.

Tertiary alcohols yield hydrocarbons (*A* and *B*) and ketones (*C* and *E*) as significant products, with the amounts of ketone formed relative to the hydrocarbons being lower than for secondary alcohols. The nature of the ketone

formed depends on the structure of the alkyl groups attached to the carbinol carbon atom. Thus, *t*-butyl alcohol yields only acetone ($I = 815$), while *t*-amyl alcohol yields acetone and methyl ethyl ketone ($I = 890$). Since *t*-butyl alcohol possesses only one type of alkyl group, acetone is formed in a relative yield which is larger than the acetone yield from *t*-amyl alcohol. However, the total relative ketone yields of the two alcohols are the same (within experimental error). Another

homologous product, *D*, is formed from these two alcohols, being the major product for *t*-amyl alcohol.

The mechanisms of alcohol photolysis under these conditions appear to be similar to those postulated for the corresponding vapor phase mercury-photo-sensitized reactions at room temperature (5–7). The important products identified for each type of alcohol under the conditions used here are identical to those found in the vapor phase reactions of simple aliphatic alcohols at room

Table I. Summary of Product Data for Aliphatic Alcohols

(Relative Peak Areas in Parentheses)

15% Carbowax 20M; $R_h = 5.7^\circ \text{C./min.}$ from 60° C.; flow rate 42.2 ml./min.

Parent compound	Retention index (<i>I</i>)						Distinctive peaks
	Homologous peaks						
Primary alcohols	<i>I</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	
Methyl	864	100 (0.33)					813 (1.00)
Ethyl	899	100 (0.05)	675 (1.00)	814 (0.21)			607 (0.02)
<i>n</i> -Propyl	1011	218 (0.16)	783 (1.00)	913 (0.02)			
<i>n</i> -Butyl	1139	309 (0.11)	878 (1.00)	1033 (0.09)			691 (0.05), 803 (0.02), 822 (0.01)
<i>n</i> -Amyl	1254	364 (0.14)	982 (1.00)	1125 (0.27)			869 (0.05), 1423 (0.07)
<i>n</i> -Hexyl	1362	437 (0.04)	1115 (1.00)	1247 (0.02)			1288 (0.60), 1328 (0.85)
Av. ΔI		834 \pm 50	246 \pm 16	107 \pm 12			
Secondary alcohols							
2-Propyl	898	272 (0.06)	812 (1.00)	1006 (0.86)			
2-Butyl	1004	218 (0.07)	892 (1.00)	1093 (4.31)			776 (0.46), 857 (0.13), 938 (0.08)
2-Amyl	1102	309 (0.03)	1009 (1.00)	1274 (10.3)			
2-Octyl	1412	517 (0.01)	1296 (1.00)	1504 (0.07)			1187 (0.13), 1345 (0.06)
Av. ΔI		778 \pm 73	102 \pm 12	−96 \pm 8			
Tertiary alcohols							
<i>t</i> -Butyl	886	100 (0.07)	430 (1.00)	815 (0.11)	991 (0.06)		673 (0.01)
<i>t</i> -Amyl	971	255 (0.02)	537 (0.07)	890 (0.03)	1085 (1.00)	814 (0.06)	938 (0.08)
Av. ΔI		751 \pm 35	445 \pm 11	76 \pm 5	−110 \pm 5		
Miscellaneous alcohols							
<i>i</i> -Butyl	1087	309 (0.40), 543 (0.01), 668 (0.02), 806 (1.00), 887 (0.15), 949 (0.08), 984 ^a , 1392 (0.22)					
Allyl	1107	364 (0.01), 717 (0.04), 843 (1.00), 998 ^a , 1393 (0.15)					
Cyclohexyl	1426	817 (0.03), 1060 (0.03), 1182 (0.92), 1350 (1.00)					

^a Offscale product peak.

temperature. The primary process therefore is the scission of the hydroxyl carbon-hydrogen bond to form intermediate species which react to form products. High molecular weight products, most likely glycols, were observed for some of the lower molecular alcohols studied. However, these heavy products were not considered for structural studies because of chromatographic difficulties involved in the analysis of these products for higher molecular weight alcohols.

ESTERS. A summary of product data for the esters studied is shown in Table II. The homologous groups of esters studied are characterized by three kinds of product peaks:

(1) Those which represent products formed within a series, each of which is a homologue. Each of these product peaks is separated from the parent peak by a value, ΔI , characteristic of that product series. The ΔI values for a particular irradiated series are characteristic and may be used to identify the type of ester of interest—i.e., ethyl, methyl, acetate, or formate ester.

(2) Common product peaks which are to be expected from an irradiated series, all of which have one part of the ester structure—e.g., the alcohol or acid moiety—in common. In some cases these common product peaks appear only for that portion of the

irradiated series in which the structures are conducive to the particular product formation. In any case the invariance of the retention index for the common product peak is characteristic of the compounds for which the peak occurs.

(3) Distinctive product peaks (not shown in Summary) which occur only for one particular compound in an irradiated series.

Each ethyl ester studied yields three product homologues, *A*, *B*, and *C*. Common product peak *E* appears for each of these esters. However, for the last two esters in the series, this product appears in low yield, while homologous product *D* is formed as the major product. Product *E* for each ester probably represents a combination of light hydrocarbon products from the alkoxy and

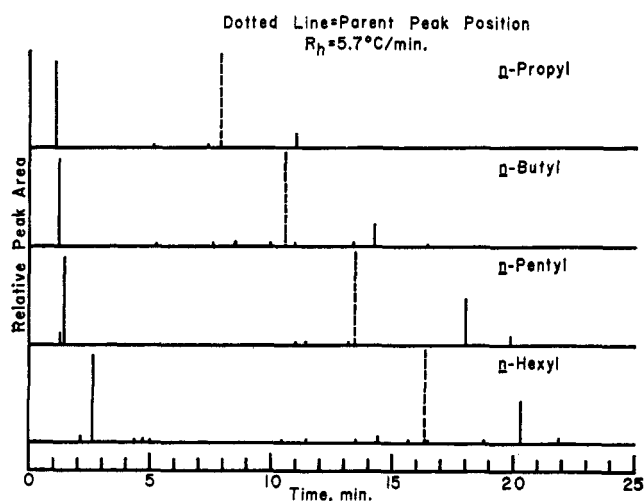


Figure 7. Chromatographic "spectra" of formates C_1 – C_7 . Irradiated 3 min.; Carbowax 20M; flow rate 42.2 ml./min.; initial temp. 60° C.

Table II. Summary of Product Data for Straight-Chain Esters

(Relative Peak Areas in Parentheses)

15% Carbowax 20M; $R_h = 5.7^\circ \text{C./min.}$ from 60° C.; flow rate 42.2 ml./min.

		Retention Index (<i>I</i>)							
		Homologous peaks				Common peaks			
Parent compound	<i>I</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	<i>G</i>	<i>H</i>
Ethyl esters									
Acetate	874	751 (0.03)	831 (0.04)	989 (1.00)		100 (0.70)	841 (0.02)		
Propionate	948	814 (0.02)	895 (0.24)	1069 (0.34)		100 (1.00)	839 (0.05)		
<i>n</i> -Butyrate	1042	948 (0.05)	995 (0.02)	1140 (0.07)		100 (1.00)	837 (0.02)	960 (0.90)	887 (0.63)
<i>n</i> -Hexanoate	1234	1105 (0.02)	1175 (0.57)	1316 (0.02)	364 (1.00)	100 (0.08)		959 (0.27)	896 (0.56)
<i>n</i> -Heptanoate	1337	1209 (0.02)	1279 (0.64)	1428 (0.86)	448 (1.00)	100 (0.07)		960 (0.18)	894 (0.54)
Av. ΔI		122 ± 11	52 ± 6	−101 ± 13	880 ± 10				
Av. <i>I</i>						100	839 ± 2	960	892 ± 4
Methyl esters									
Acetate	824		906 (1.00)	995 (0.31)		100 (0.17)			
Propionate	884		999 (1.00)	1026 (0.08)		100 (0.15)			
<i>n</i> -Butyrate	967	819 (0.01)	1071 (0.45)	1185 (0.07)		100 (1.00)	836 (0.37)	959 (0.01)	1128 (0.02)
<i>n</i> -Hexanoate	1169	1115 (0.04)	1281 (0.50)	1385 (0.49)	381 (1.00)		847 (0.39)	971 (0.07)	1127 (0.03)
Av. ΔI		57 ± 5	−103 ± 10	−202 ± 20					
Av. <i>I</i>						100	841 ± 6	965 ± 6	1128
Acetates									
Methyl	824					100 (0.20)	995 (0.31)		
Ethyl	874		751 (0.03)			100 (0.70)	989 (1.00)		
<i>n</i> -Propyl	970	273 (1.00)	874 (0.05)			100 (0.02)			
<i>n</i> -Butyl	1070	400 (0.09)	986 (1.00)	1140 (0.02)			1004 (0.02)		
<i>n</i> -Hexyl	1271	595 (0.97)	1177 (0.09)	1357 (0.26)	1251 (0.17)		995 (0.29)	1090 (1.00)	1211 (0.09)
<i>n</i> -Heptyl	1370	739 (1.00)	1286 (0.28)	1459 (0.35)	1348 (0.08)		1001 (0.03)	1097 (0.05)	1220 (0.09)
Av. ΔI		666 ± 26	94 ± 12	−81 ± 7	21 ± 1				
Av. <i>I</i>						100	997 ± 5	1094 ± 4	1216 ± 5
Formates									
		Homologous peaks							
		<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>		
<i>n</i> -Propyl	903	318 (1.00)	833 (0.01)	882 (0.02)	1023 (0.16)				
<i>n</i> -Butyl	1007	410 (1.00)	928 (0.04)	985 (0.03)	1137 (0.26)	1214 (0.02)	891 (0.01)		
<i>n</i> -Pentyl	1109	453 (1.00)	1037 (0.02)	1099 (0.02)	1272 (0.53)	1340 (0.09)	1023 (0.02)		
<i>n</i> -Hexyl	1211	626 (1.00)	1142 (0.06)	1186 (0.01)	1356 (0.48)	1415 (0.05)	1111 (0.02)		
Av. ΔI		606 ± 20	70 ± 3	19.5 ± 5	−140 ± 15	−214 ± 11	101 ± 10		

acyl portion of each ester, since the lower molecular weight hydrocarbons are not well separated on Carbowax 20M under these conditions. Since the relative area of this peak for the latter two esters in the series is small, product *D* represents a light hydrocarbon homologous series, the lower members of which are included in peak *E* for the first three esters. Therefore, the acyl portion of the ethyl esters studied is predominant in the formation of products *D* and *E*. Common product *F* is formed from the first three ethyl esters in the series, while products *G* and *H* are formed from the ethyl esters containing hydrogens gamma to the carbonyl in the acyl group.

Unique photolytic reactions occurring for straight-chain alkyl esters containing gamma-hydrogens in the acyl group were proposed by Ausloos (*1*). Such esters react by direct photolysis at lower wavelengths to yield an acetate ester and an olefinic hydrocarbon with two less carbon atoms than the acyl group. Product *H* corresponds to ethyl acetate, which is the expected product of ethyl esters undergoing such a reaction.

Each methyl ester studied yields two homologous products (*B* and *C*), with *B* being a significant product. Product *A* is formed for each of these esters except methyl acetate. A product, *E*, appears for each of the methyl esters studied except for methyl *n*-hexanoate, which produces the major product *D*. Product peak *E* is of approximately equal relative size for methyl acetate and methyl propionate, while for the other two methyl esters *E* and *D*, respectively, are the major products. Product *D* agrees in retention closely with product *D* of ethyl *n*-hexanoate, as expected, since the acyl portions of ethyl *n*-hexanoate and methyl *n*-hexanoate are identical. The low yield of the light product, *E*, for the first two methyl esters listed indicates that the ethoxyl group is more predominant in light hydrocarbon product formation than is the methoxyl group of an ester, since the product *E* for ethyl acetate and ethyl propionate is the major one. The common products, *F*, *G*, and *H*, are formed from the methyl esters having hydrogens gamma to the carbonyl in the acyl group.

Product *F* corresponds to methyl acetate, which is the product expected by the previously discussed mechanism from methyl esters containing hydrogens gamma to the carbonyl in the acyl group.

Acetates form characteristic homologous products *A* through *D*. The product *E* appears for the first three acetates listed and is absent for the latter three. Product *A* formed for each acetate containing gamma-hydrogens in the alkoxyl alkyl group. This

product series is probably a continuation of the series of which product *E* for ethyl acetate is the first member. Product *C* appears for the latter three esters listed as does product *D* for the latter two acetates studied. Product *F* appears for all the acetates studied, with its position being covered by the offscale parent peak of irradiated *n*-propyl acetate. Products *G* and *H* appear for the latter two acetates listed.

The formates yield only homologous products with a light hydrocarbon *A* as the major product and the corresponding alcohol *D* as the second most abundant product. Thus, each formate may be expected to yield its precursor alcohol as its second most abundant product. Minor products *B* and *C* are formed for each formate, while minor products *E* and *F* are formed only for the latter three formates studied.

Thus, both the acyl and alkoxyl portion of an ester are important in product formation. This is seen from the systematic homologous and common product formation within each ester series in which either the acyl or alkoxyl portion is common while the chain length of one part varies.

Although no attempt was made to identify all the products shown in Table II, some definite conclusions concerning the modes of product formation may be made. The formation of light hydrocarbon products is important and characteristic of both the alkoxyl and acyl ester moieties. Since these and other products observed are also prevalent in the direct liquid phase photolysis of some simple alkyl esters at shorter wavelengths (*1*), intramolecular processes as well as direct scission of bonds are the principal primary reactions of the esters studied under the conditions used here.

Irradiation of Mixtures. Mixtures of ethanol and isopropyl alcohol were irradiated with the mercury resonance radiation. The formation of irradiation products from both compounds was greatly suppressed below the yields obtained from the respective pure compounds. The suppression of products is to be expected, since free radicals formed in the primary process for each compound can react with the free radicals of the other as well as the other substrate itself, thus reducing the probability of each compound forming products by its own mechanism. The higher yield products for the two compounds individually would tend to take precedence in a competing environment, and the relative yields of individual products depend upon the relative amount of parent present in the original mixture. The suppression of products varied as the relative amounts of ethanol and isopropanol were changed.

Another phenomenon influencing the

speed and extent of reaction of compounds in a mixture is the relative selectivity of the excited mercury attack on the compounds involved. The differences in selectivity would be more pronounced in a mixture composed of compounds containing different functional groups. Therefore, the technique described here is best suited for the qualitative identification and study of small amounts of pure compounds.

Effect of Irradiation Time. The relative distributions of products as a function of irradiation time for some typical alcohols and esters changed relatively little over large irradiation time ranges. In such a study for ethanol, isopropyl alcohol, and *t*-butyl alcohol the largest relative change of any product was approximately 8-fold over a 12-fold range in irradiation time. In a similar study of the lighter products of ethyl acetate, the largest relative change was less than 10-fold over a 10-fold range in irradiation time. In all the cases studied the identity of the major product remained unchanged throughout the irradiation time ranges used. In the cases of ethanol, isopropyl alcohol, and ethyl acetate, there were ranges of irradiation times over which the relative product distributions changed very little, indicating that quantitative results may be reproduced easily in these ranges.

Effect of Sample Size. The number and positions of product peaks are independent of sample size over at least a 4-fold range of sample sizes. The minimum sample size which may be handled with reproducible results is limited by the size of the irradiation capillary. In this study, samples less than 1.0 mg. in size in the liquid state showed somewhat erratic results. Reproducible amounts of irradiation products were obtained when the sample size was maintained in the range 1.0–2.0 mg.

Effect of Deaeration. Several samples of isopropyl alcohol were irradiated for 3 minutes without prior deaeration and compared to those which had been deaerated. Only a short-duration vacuum was drawn on the sample headspace before sealing to remove traces of moisture-containing air. The product yields were observed to be quite inhibited and very erratic. Since oxygen is known to act as an inhibitor in photochemical reactions, these observations were expected and justify the need for prior deaeration of samples.

Choice of Retention Index as a Retention Parameter. Programmed temperature retention indices were introduced by Van Den Dool and Kratz (*14*). This retention parameter is independent of temperature program rate, carrier gas flow rate, liquid phase

weight, and apparatus dead volume for a solute on a given liquid phase. It is assumed that the isothermal temperature dependence of the retention index is negligible over a range of retention temperatures which might be obtained for different programs. This assumption is valid for the vast majority of solutes, as shown by the data of Kovats (8) and Wehrli and Kovats (15), who introduced the use of the retention index for isothermal gas chromatography.

Retention indices were obtained for some esters, alcohols, aldehydes, and ketones on each of the two columns used under the conditions of this study. These indices were then compared to those obtained for the same compounds on Carbowax 20M by Van Den Dool and Kratz (14). These authors used a 20% liquid phase loading, a program rate of 4.6° C./minute in the range 75°–228° C., and a carrier gas flow rate of 80 ml./minute.

When compared with those values previously reported in the literature, agreement was to within $\pm 1\%$ with rare exception, and the values obtained on the columns used in this study agree to within $\pm 0.5\%$. Programmed temperature retention indices reported in this work are therefore suitably reproducible retention parameters for use with Carbowax 20M. Retention indices below 600 are somewhat difficult to measure with accuracy, owing to the short retention time for the lower hydrocarbon standards on a Carbowax 20M column.

The validity of assuming constant ΔI values for homologous products was

confirmed by plotting the foregoing calculated retention indices vs. chain length for each of the series. The plots are remarkably linear and parallel to each other and to the plot for normal paraffins, which is linear by definition. Some deviation from linearity was noted at low carbon numbers for only a few of these functional groups. Such deviations for product homologous series would serve to increase the scatter of the resulting ΔI values for the lower members of the irradiated series.

CONCLUSIONS

The method proposed here is suitable for the qualitative identification of small amounts of pure organic compounds. Since homologous and/or common products are formed within each irradiated series, products to be expected from previously unstudied members of the series may be predicted.

Solids may be difficult to study by this technique because of the relatively small absolute energy of a steady-state mercury discharge. This might be overcome through the use of flash photolysis, which would produce high instantaneous radiant energy and reduce the analysis time.

Liquid phase photolysis requires samples of the order of 1 mg., whereas pyrolysis–GLC is applicable to samples in the microgram range.

Photolytic degradation–GLC is a technique which holds promise as a complementary method for the identification and study of organic compounds.

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Sensitive Selective Gas Chromatography Detector Based on Emission Spectrometry of Organic Compounds

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► A gas chromatography detector has been developed which is based on monitoring the intensity of the electronic emission spectra of the eluted organic compounds in an argon carrier gas. The spectra are excited in the plasma of a 2450-Mc. electrodeless discharge and detected photoelectrically in the ultraviolet-visible region. The detector sensitivity is 2×10^{-16} gram of hexane per second. By choosing the wavelength of various atomic lines and molecular bands, a degree of selectivity can be obtained.

The system can be sensitized to the halogens, phosphorus, and sulfur, as well as permanent gases. The detector has a high sensitivity and selectivity, a small volume, rapid response, and a wide dynamic range.

ELECTRONIC spectra emitted from electrical discharges through gases have been studied since the early beginnings of spectrometry. Such plasma sources have been used frequently to obtain information on spectrometric constants and much of the information

on the spectra of diatomic molecules has been obtained from this technique (6). However, very few analytical methods have been developed, and this paper suggests some possible applications.

The red band spectrum of nitrogen excited by a spark coil is widely used as a leak detector in vacuum systems. Fay, Mohr, and Cook (2) studied the efficiencies of various types of electrical discharges in exciting the emission spectrum of traces of nitrogen in argon. The intensity of the emitted spectrum could thus be used to determine very low