TABLE II

CHARACTERISTIC THERMAL AND X-RAY DIFFRACTION DATA

	EEE	PEE	SEE	PEP	SES	EPE	ESE	PePePe	PPePe	SPePe	PPeP	SPeS
M.p., °C.												
Alpha	15.3	22.8	28.8	36.8	42.9	26.0	34.0	18.8	26.4	31.5	35.9	43.4
Beta prime		33		53.2	47	32.0	43.2		35.9		54.3	
Beta	42.4	40.3	49.6	53.3	59.5	44.5	50.1	52.5	46.4	55.0	54.9	62.6
X-Ray data: long spacings, Å.												
Alpha	49.6	48.8	50.5	45.5	50.8	48.6	48.7	49.5	48.9	50.5	47.5	50.8
Beta prime		44.3		43.0	46.9	44.1	45.9		45.3		42.7	
Beta	44.6	44.1	44.75	42.05	45.0	43.2	44.8	44.6	43.4	44.6	41.7	44.8
Short spacings, Å.												
Alpha	4.15S	4.15S	4.15S	4.15S	4.15S	4.12S	4.12S	4.15S	4.12S	4.13S	4.13S	4.13S
Beta prime		4.18S		4.20S	4.36S	4.09S	4.2S(diff.)		4.21S		4.20S	
					4.16S							
		3.83M		3.85M	3.82M	3.81S−	3.82S−		3.86M		3.82S	
Beta	5.6W	5.32M	5.25W	5.30M	5.35W	5.30W+	5.34M	5.32W	5.34W	5.34M	5.32M	5.45W
	4.58S	4.60VS	4.87W	4.60S+	4.61S	4.58S+	4.56S	4.56S	4.55S	4.55S	4.58S	4.58S
	3.93M	3.90M	4.56S	3.87S−	3.90S−	3.82S+	3.87S	3.88M	3.86S	3.86S	3.82S	3.87M
	3.71M	3.72M	3.91M	3.78S	3.75S−		3.63S	3.80S	3.80S	3.77S		3.75M
			3.70W+									

TABLE III

STABILITY OF VARIOUS FORMS OF GLYCERIDES

U, unstable; S, stable; V, very; M, moderately; MM, more than moderately

EEE	PEE	SEE	PEP	SES	EPE	ESE
Elaidyl glycerides						
α(U)	α(U)	α(MMS)	α(MS)	α(U)	α(MS)	α(U)
....	β'(MS)	......	β'(S)	β'(U)	β'(MS)	β'(MS)
β(S)	β(S)	β(S)	β(S)	β(S)	β(S)	β(S)
Petroselaidyl glycerides						
PePePe	PPePe	SPePe	PPeP	SPeS		
α(VU)	α(U)	α(U)	α(U)	α(MS)		
....	β'(U)	......	β'(MMS)	....		
β(S)	β(S)	β(S)	β(S)	β(S)		
Comparable stearyl glycerides						
SSS	PSS	SSS	PSP	SSS	SPS	SSS
α(U)	α(U)	α(U)	α(VU)	α(U)	α(MMS)	α(U)
β'(VU)	β'(S)	β'(VU)	β'(S)	β'(VU)		β'(VU)
β(S)	β(S)	β(S)		β(S)	β(S)	β(S)

above the elaidyl glycerides by about 3° for each chain difference. The present m.p. value for PEE, 6° lower than the literature, seems definitely better in line with values for related compounds. Moreover, one of the present PEE preparations was hydrogenated to an authentic PSS of m.p. 65.0°.[3]

It is interesting to compare EEE and PePePe in the light of known differences in their fatty acid m.p.'s, 45.5° and 53.6°[9] for elaidic and petroselaidic, respectively. The glycerides in their tilted stable forms shows as much difference, but in their perpendicular alpha forms show only 3° m.p. difference. It is suggested that a m.p. alternation[10] occurs in the case of stable forms of *trans*-octadecenoic glycerides as for the corresponding acids, but a lesser alternation or perhaps none is anticipated for non-tilted alpha forms.

Acknowledgment.—The authors wish to express their appreciation to Mr. R. G. Folzenlogen for the synthesis of these compounds and to Mrs. R. M. Foltzer for much of the experimental work.

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[9] W. F. Huber, THIS JOURNAL, **73**, 2730 (1951).

[10] An alternation in m.p. between compounds with double bond in "odd" position, *e.g.*, *trans* 9-octadecenoic (elaidic), and compounds with double bond in "even" position, *e.g.*, *trans*-6-octadecenoic (petroselaidic) compounds.

CINCINNATI 31, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARKANSAS]

A Tracer Study of the Reaction of Isocyanates with Carboxylic Acids[1,2]

BY ARTHUR FRY

RECEIVED DECEMBER 29, 1952

By the use of C^{14}-carboxyl labeled acids, the carbon dioxide evolved during the reaction of isocyanates with carboxylic acids has been shown to come from the isocyanate. In a similar manner, the carbon dioxide produced from the reaction of carbanilide with acetic anhydride has been shown to come from the carbanilide.

The reaction between isocyanates and carboxylic acids may proceed by two different paths.[3]

$$RNCO + R'COOH \longrightarrow CO_2 + R'CONHR \quad (1)$$

$$2RNCO + 2R'COOH \longrightarrow CO_2 + (R'CO)_2O + (RNH)_2CO \quad (2)$$

A mixture of products corresponding to partial reaction by both paths is usually obtained. The products from reaction (2), the carboxylic acid anhydride and the urea, have been shown to undergo further reaction at higher temperatures to give carbon dioxide and two moles of the amide, R'CONHR.[3]

Dieckmann and Breest[4] showed that the first product obtained from the reaction of isocyanates with carboxylic acids was the mixed carbamic acid–carboxylic acid anhydride of the general formula

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[1] This work was supported in part by the A.E.C.

[2] Presented at the Eighth Southwest Regional American Chemical Society Meeting, Little Rock, Arkansas, December 4–6, 1952.

[3] C. Naegeli and A. Tyabji, *Helv. Chim. Acta*, **17**, 931 (1934); **18**, 142 (1935); and earlier references cited there.

[4] W. Dieckmann and F. Breest, *Ber.*, **39**, 3052 (1906).

R'COOCONHR. These mixed anhydrides are relatively unstable, but in some cases[3,4] they have been isolated and analyzed. The mixed anhydrides, either in the solid state or in solution, decompose further to give the products of reactions (1) and (2) above.

This mixed anhydride might lose carbon dioxide, giving the N-substituted amide as in equation (1). If this addition compound is an intermediate in either reaction (1) or (2), it is conceivable that either of its carbonyl groups could be lost as carbon dioxide. Kraft and Karstens[5] studied the reaction of benzoic acid with phenyl isothiocyanate, and found that carbon oxysulfide was evolved. Thus, if isocyanates and isothiocyanates behave in a similar manner, the carbon dioxide evolved would be expected to come from the isocyanates.

In order to establish unequivocally the source of the carbon dioxide evolved in the reaction of isocyanates with carboxylic acids, two different isocyanates were allowed to react with each of two different C^{14}-carboxyl labeled acids, and the activity distribution in the resulting products studied. The results are shown in Table I. The indicated errors represent the over-all reproducibility of combustion, sample preparation and radioactivity determination.

TABLE I

RELATIVE MOLAR ACTIVITIES OF PRODUCTS FROM THE REACTION OF INACTIVE ISOCYANATES WITH C^{14}-CARBOXYL LABELED ACIDS (MOLAR ACTIVITY = 100[a])

Expt. no.	R' in $R'C^{14}OOH$	R in RNCO	Relative molar activities of products CO_2	R'CONHR	$(RNH)_2$
1	CH_3	C_6H_5	0.0 ± 0.22	99.5 ± 2.0	0.0 ± 0.27
2	CH_3	*p*-BrC_6H_4	.0 ± .22	98.2 ± 2.0	.3 ± .27
3	$C_6H_5CH_2$	C_6H_5	.0 ± .12	99.2 ± 2.0	.0 ± .27
4	$C_6H_5CH_2$	*p*-BrC_6H_4	.96 ± .20	101.7 ± 2.0	.0 ± .27

[a] Actual activity: $CH_3C^{14}OOH$, 1.86 × 10^8 d.m./mole; $C_6H_5CH_2C^{14}OOH$, 3.39 × 10^8d./m./mole.

The N-substituted amide obtained from the reaction has the same molar activity as the acid used, while the carbon dioxide and the substituted urea are essentially inactive. Therefore, the conclusion is drawn that the carbon dioxide evolved in the reaction of isocyanates with carboxylic acids comes from the isocyanate and not from the acid. This conclusion is in line with the behavior of isocyanates with other active hydrogen compounds, and with the work of Kraft and Karstens mentioned above.

The reaction between inactive carbanilide and acetic anhydride-1-C^{14} at 135° was also studied (experiment 5). Assigning the acetyl group of the acetic anhydride a relative molar activity of 100, the carbon dioxide evolved has a relative molar activity of 0.38, while the acetanilide has a relative molar activity of 100.0. Thus it is seen that in this reaction too, the carbonyl group of the amide comes from the acid anhydride and the carbon dioxide comes from the carbonyl group of the substituted urea.

The presence of the small amount of activity in the 4,4'-dibromocarbanilide in experiment 2 is probably due to insufficient purification. In this case, due to the small size of the sample, only two recrystallizations were carried out instead of the usual three or four. The presence of activity in the carbon dioxide in experiment 4 is real. The value obtained is considerably greater than the experimental error, and the experiment was repeated several times with very similar results. This activity may be due to a small amount of acylative decarboxylation of the phenylacetic acid-1-C^{14}, such as occurs in the Dakin–West reaction.[6] This type of reaction may also explain the small amount of activity found in the carbon dioxide in the reaction between carbanilide and acetic anhydride-1-C^{14}.

Experimental

Materials.—Conventional methods were used in the preparation of the labeled acetic acid,[7] phenylacetic acid[8] and acetic anhydride.[9] The isocyanates were commercial products and were distilled or recrystallized before use.

Experimental Procedure.—The reactions were carried out in a sweep system consisting of a purification train, the reaction vessel, a trap at −80° and a spiral bubbler. After flushing the system with dry carbon dioxide-free air, 1 *M* carbonate-free sodium hydroxide was introduced into the spiral bubbler. Equal molar quantities (approximately 0.01 mole) of the acid and the isocyanate were washed into the reaction vessel with 5 ml. of benzene or xylene. The system was swept with dry, carbon dioxide-free air until carbon dioxide was no longer evolved. The time necessary for complete carbon dioxide evolution had been previously established by inactive runs. In experiments 1 and 2 the reaction vessel was placed in a bath of vapor from boiling benzene (80°). Experiments 3 and 4 were run at room temperature. After reaction was complete the carbon di-

TABLE II

MELTING POINTS OF REACTANTS AND PRODUCTS AND SPECIFIC ACTIVITIES OF BARIUM CARBONATE OBTAINED FROM COMBUSTION OF THESE REACTANTS AND PRODUCTS

Expt. no.	Compound	M.p., °C.	Lit. m.p., °C.	Specific activity, d./m./mg. $BaCO_3$
1 and 2	Acetic-1-C^{14} acid	....	....	472 ± 9.5
3 and 4	Phenylacetic-1-C^{14} acid	76–76.5	76[a]	214 ± 4.3
1–3	Carbon dioxide	....	....	<0.2 ± 0.2
4	Carbon dioxide	....	....	16.5 ± 0.33
1	Acetanilide	113–114	114[a]	117 ± 2.3
2	*p*-Bromoacetanilide	164–165	167[a]	116 ± 2.3
3	α-Toluanilide	117–118	117[a]	122 ± 2.4
4	4'-Bromo-α-toluanilide	174–175[b]		125 ± 2.5
1 and 3	Carbanilide	237.5–238	238[a]	<0.2 ± 0.2
2	4,4'-Dibromocarbanilide	300–305	300–330[c]	0.23 ± 0.2
4	4,4'-Dibromocarbanilide	310–320	300–330[c]	<0.2 ± 0.2
5	Acetic-1-C^{14}-anhydride	....	....	332 ± 6.6
5	Carbon dioxide	....	....	2.5 ± 0.2
5	Acetanilide	113–114	114[a]	82.5 ± 1.6

[a] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948. [b] Needles from benzene–cyclohexane or ether. *Anal.* Calcd. for $C_{14}H_{12}NOBr$: C, 57.95; H, 4.17. Found: C, 57.80; H, 4.22. [c] H. Blitz, *Ann.*, 368, 156 (1909), reports that this compound darkens at 300°, is black at 320° and dec. at *ca.* 330°.

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[5] F. Kraft and H. Karstens, *ibid.*, **25**, 452 (1892).

[6] H. Dakin and R. West, *J. Biol. Chem.*, **78**, 91 (1928).

[7] M. Calvin, C. Heidelberger, J. Reid, B. Tolbert and P. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 177.

[8] H. Gilman and A. Blatt, "Organic Syntheses," Coll. Vol. I, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 436.

[9] S. Ruben, M. Allen and P. Nahinsky, THIS JOURNAL, **64**, 3050 (1942).

oxide was precipitated as barium carbonate and weighed. The yield of carbon dioxide amounted to from 0.6 to 0.8 mole per mole of acid or isocyanate, corresponding to varying ratios of reaction according to equations (1) and (2).[10] The residue in the reaction vessel was filtered and the residue extracted with hot ether and hot benzene to remove the anhydride, any unreacted acid and isocyanate and the substituted amide. The residual substituted urea was recrystallized several times from alcohol in the case of carbanilide or glacial acetic acid in the case of 4,4'-dibromocarbanilide. The filtrate containing the amide was extracted with 10% sodium carbonate solution and the organic layer evaporated to dryness. The resulting crude amide was recrystallized several times from a suitable solvent. In all cases the melting points of the purified products agreed with the literature values as shown in Table II. Samples of the substituted amide and urea and of the labeled acids and anhydride used were quantitatively oxidized to carbon dioxide by a wet combustion procedure.[11] The carbon dioxide was absorbed in sodium hydroxide and precipitated as barium carbonate. All samples were counted as barium carbonate plates using an internal flow counter[12] operated in the Geiger region. Appropriate corrections were made for self-absorption. The geometry of the counting system was established by counting barium carbonate plates prepared from a National Bureau of Standards sodium carbonate-C^{14} sample of known disintegration rate. The specific activity of the barium carbonate from each of the reactants and products is given in Table II.

Acknowledgments.—The author wishes to acknowledge an interesting discussion with Dr. S. H. Lee at the inception of this work, and the help of Mr. R. Childers and Mr. W. Carrick in the preparation of some of the radioactive compounds and in some of the preliminary experiments.

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(10) If the reaction vessel was heated to about 135° and the reaction continued, the yield of carbon dioxide calculated from equation (1) became practically quantitative. This is undoubtedly due to the further reaction of the anhydride and substituted urea mentioned above.

(11) A. Fry, B. M. Tolbert and M. Calvin, University of California Radiation Laboratory Report, UCRL 1570 (1951).

(12) P. Damon, *Rev. Sci. Instruments*, **22**, 587 (1951).

FAYETTEVILLE, ARKANSAS

[CONTRIBUTION FROM THE ILLINOIS STATE GEOLOGICAL SURVEY]

Coal Oxidation. Comparative Studies on Phenols[1]

BY G. R. YOHE, D. R. HILL, J. E. DUNBAR AND F. M. SCHEIDT

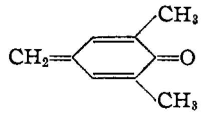
RECEIVED JANUARY 17, 1953

Twelve phenols were subjected to oxidation with gaseous oxygen in the presence of aqueous sodium hydroxide under conditions previously applied to coals. Oxygen absorption rate curves are shown, and compared with curves obtained from coals. A study of the oxidation products shows that oxidative condensations as well as degradations have occurred; 3,5,3',5'-tetra-*t*-butyl-4,4'-dihydroxy-1,2-diphenylethane and 3,5,3',5'-tetra-*t*-butylstilbene-4,4'-quinone were identified as alkali-insoluble oxidation products of 2,6-di-*t*-butyl-4-methylphenol. It is suggested that such oxidative condensations may play a part in the formation of "humic acids" when coals are oxidized.

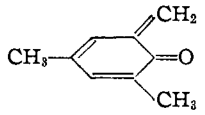
In a study of the effect of methylation with dimethyl sulfate on the oxidation characteristics of coals, evidence was obtained which indicated that coals up to and including the high-volatile bituminous ranks contain appreciable amounts of phenolic structure.[2] Application of the same oxidation procedure to various types of pure organic compounds showed that the oxygen absorption rate curves for certain phenols resembled those of the coals.

The present paper reports the results obtained by the oxidation of twelve phenols under the same experimental conditions, and includes a detailed study of the alkali-insoluble oxidation products from 2,6-di-*t*-butyl-4-methylphenol.

The possibility that the oxidation of phenols might proceed by way of quinones was considered, yet early in the work it was found that certain of the alkyl substituted phenols oxidized more rapidly than did phenol itself. The fact that simple quinones could not be formed in all cases (*i.e.*, the 2,4,6-trialkylphenols) unless dealkylation occurred first led to the suggestion that intermediates of the methylene quinone type[3] might be involved.

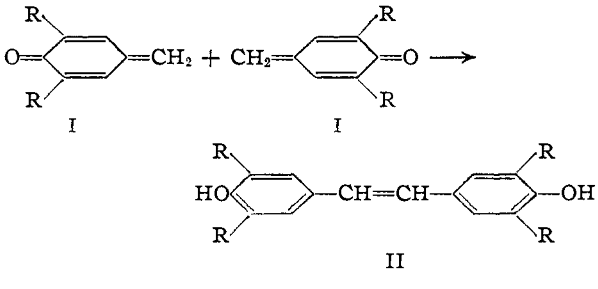


I



Ia

Attempts to isolate simple methylene quinones have not been successful, but have led to di- or trimeric products.[4-7] The dimerization of 4-methylene quinones (I) has been depicted[6] as a direct combination to form the dihydroxystilbene (II, R = CH_3)



but v. Euler[8] concluded that a disproportionation occurred forming the stilbenequinone (III) and the diphenylethane derivative IV (R = CH_3)

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(1) Presented before the Division of Gas and Fuel Chemistry, American Chemical Society, Atlantic City, N. J., September 15, 1952. Published with permission of the Chief, Illinois State Geological Survey.

(2) G. R. Yohe and Eva O. Blodgett, THIS JOURNAL, **69**, 2644 (1947).

(3) An excellent summary and review of the literature on methylene quinones has been published in "Chemie der Phenolharze," by K. Hultzsch, Springer-Verlag, Berlin-Göttingen-Heidelberg, 1950, Chapter V, pp. 63–87.

(4) T. Pummerer and E. Cherbuliez, *Ber.*, **52**, 1392 (1919).

(5) K. Fries and E. Brandes, *Ann.*, **542**, 48 (1939).

(6) K. Hultzsch, *Ber.*, **74**, 898 (1941).

(7) K. Fries and K. Kann, *Ann.*, **353**, 335 (1907).

(8) H. v. Euler, E. Adler, J. O. Cedwall and O. Törngren, *Arkiv Kemi, Mineral. Geol.*, **15A**, No. 11, 1 (1942).