changed on admixture with an authentic sample of hexachloroethane.

Anal. Calcd. for C_2Cl_6: Cl, 89.9. Found: Cl, 89.4.

Catalysis of Polymerization of Ethenoid Monomers by Peroxydicarbonates.—Monomeric styrene, vinyl acetate and methyl methacrylate from commercial sources were redistilled before use.

2,2′-Oxydiethylene bis-(allyl carbonate), *i. e.*, the bis-(allyl carbonate) of diethylene glycol,[37] was prepared[38] by the addition of 1326 g. (11.0 moles, 10% excess) of allyl chloroformate to an efficiently stirred mixture of 531 g. (5.0 moles) of diethylene glycol and 949 g. (12.0 moles) of pyridine, cooling to keep the reaction mixture at 5-10°. After the addition was complete, the reaction mixture was allowed to warm to room temperature, diluted with an equal volume of water and neutralized to the methyl orange end-point using dilute hydrochloric acid. The crude oily ester was separated, washed with an equal volume of cold 2% aqueous hydrochloric acid, once with an equal volume of cold 2% aqueous sodium hydroxide then twice further with cold water. The crude product was dried over sodium sulfate, and purified by distillation with a small stream of carbon dioxide passing through the ester. The yield was 1030 g. (75%) of colorless 2,2′-oxydiethylene bis-(allyl carbonate), b. p. 160° (2 mm.), n^{20}_D 1.4503, d^{20}_4 1.143.

Anal. Calcd. for $(C_3H_5OCOOC_2H_4)_2O$, $C_{12}H_{18}O_7$: C, 52.5; iodine number,[39] 185.1. Found: C, 52.2; iodine number, 185.1.

A loss of about 15% due to polymerization during distillation was avoided in other preparations by heating the crude ester at 150° *in vacuo* (5-10 mm.) for removal of volatile impurities, the product obtained being 97-99% pure by unsaturation analysis.

Diisopropyl peroxydicarbonate was dissolved in these monomers in the following percentages by weight, based on the monomer: styrene 0.5%, vinyl acetate 0.1%, methyl methacrylate 0.2%, 2,2′-oxydiethylene bis-(allyl-carbonate) 3.0%. Two-ml. samples of the solutions were heated under nitrogen in closed test-tubes (10 mm. × 75 mm.) for three days at 45° then cooled to room temperature. Hard, colorless, solid polymers were obtained in all cases.

Summary

1. Dialkyl and substituted dialkyl peroxydicarbonates (Type I peroxycarbonates) may be prepared readily, often in good yields and high purity, from the corresponding chloroformates and sodium peroxide solutions. Most of these esters in pure form are unstable, decomposing, in some cases explosively, at normal temperatures. Appropriate temperature control in preparation and handling is accordingly required.

2. Wide differences in thermal stability in pure form are observed among esters of Type I, depending upon the alkyl or substituted alkyl group. Similarly wide differences in stability are observed in solutions of a given ester depending upon the nature of the solvent used. The thermal decomposition of the more unstable esters is retarded by known inhibitors of chain reactions, and yields a complex mixture of products characteristic of chain decompositions. In dilute solutions in selected solvents the wide differences in decomposition rates are no longer observed, and the decompositions conform closely to first order kinetics. The thermal decomposition of the different esters is thus shown to consist of a spontaneous unimolecular decomposition, with the formation of free radicals which induce concurrent chain decomposition reactions of the esters to different extents depending upon the particular ester and solvent involved. These chain decompositions are similar to those known to occur in benzoyl peroxide solutions.

3. Examples of the related esters of monoperoxycarbonic acid (Type II) and of diperoxycarbonic acid (Type III) have also been prepared; these esters are more stable than the esters of Type I.

4. Many of the esters of Type I are effective free radical type catalysts for polymerization of typical ethenoid monomers at moderate temperatures.

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[37] Muskat and Strain, U. S. Patent 2,370,565, Feb. 27, 1945.

[38] Muskat and Strain, U. S. Patent 2,370,567, Feb. 27, 1945.

[39] Hanus method, Jamieson, "Vegetable Fats and Oils," A. C. S. Monograph No. 58, Second Edition, (The Chemical Catalog Co., Inc.) Reinhold Publ. Corp., New York, N. Y., 1943, p. 394.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Heats of Combustion of Some Isomeric Nitrostilbenes[1]

BY CARL M. ANDERSON,[2a] LELAND G. COLE[2b] AND E. C. GILBERT

For a number of years this Laboratory has been interested in energy relations of isomeric organic compounds as obtained from heats of combustion.[3]

Through the courtesy of Prof. Melvin Calvin, it has now been possible to obtain two additional pairs of carefully purified isomers, *cis*- and *trans*-4,4′-dinitrostilbene, and *cis*- and *trans*-4-mononitrostilbene, (unsym. *p*-nitrostilbene). Measurements of the heat of combustion of these four compounds are reported here, and the energies of isomerization in the solid state are indicated.

Experimental

The adiabatic calorimeter has been previously described.[3] The energy equivalent was determined by the combustion of benzoic acid Standard Sample, 39e, from the National Bureau of Standards, by Anderson who obtained 2607.30 cal. deg.$^{-1}$ with a maximum deviation of 1.45 cal. from the mean, a mean deviation of ±0.56 cal., and a root-mean-square deviation of ±0.28 cal. After approximately a year a redetermination by Cole using Standard 39f, gave 2607.34 cal. deg.$^{-1}$ with a mean deviation of

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[3] Corruccini and Gilbert, THIS JOURNAL, **61**, 2925 (1939); Davies and Gilbert, *ibid.*, **63**, 1585, 2730 (1941); Anderson and Gilbert, *ibid.*, **64**, 2369 (1942).

±0.62 cal. from the mean. These results are expresssed in defined calories such that 4.1833 int. joules equals 1 defined calorie. The precision obtainable under optimum conditions with this instrument is 0.01–0.02%.

Materials.—*cis*-4-Mononitrostilbene was prepared by W. W. Miller of the Univ. of California, at Berkeley, and melted at 59.5–61.0°. *trans*-4-Mononitrostilbene was likewise prepared by Mr. Miller and melted at 157.5°. *cis*-4,4′-Dinitrostilbene had a melting point of 303–304°, having been recrystallized from benzene. *trans*-4,4′-Dinitrostilbene melted at 186.0–186.5°, and had been recrystallized from acetone. All samples were dried over phosphorus pentoxide for two days *in vacuo* before making into pellets. They were not purified further.

Calculations.—All weights are reported *in vacuo*. The data are referred to a standard temperature of 25°. From the results was calculated first $-\Delta U_B$, the heat experimentally evolved in the bomb process per gram formula weight of compound burned to form carbon dioxide, water and nitrogen. From this was obtained $-\Delta U_R$, the decrease in energy for the combustion reaction to form these products in the standard state of constant volume, as defined by Washburn.[4] In making this calculation it was assumed that nitrogen produced in the reaction may be treated as if it were oxygen and the correction quantities appropriately modified. $-\Delta H_R$ the heat evolved in the isothermal process in the standard state at constant pressure (1 atmosphere) was also calculated. Tabulated also are the standard heats of formation of these compounds in the solid state at 25°.

TABLE I

HEAT OF COMBUSTION

True mass of sample, g.	Temp.,[a] °C.	Total[a] heat, cal.	Heat from HNO_3, cal.	$-\Delta U_B/m$, cal./g.	Dev. from mean
		cis-4-Mononitrostilbene			
0.43349	1.2100	3318.7	5.21	(7643.8)	...
.30884	0.9060	2365.6	3.26	7649.2	−2.3
.30840	.9051	2363.1	3.17	7652.2	+0.7
.26813	.7870	2054.8	2.69	7653.6	+2.1
.35796	1.0503	2742.4	3.58	7651.1	−0.4
			Mean	7651.5	±1.4
		trans-4-Mononitrostilbene			
0.57439	1.6791	4384.5	7.32	7620.5	−0.3
.44422	1.2978	3388.7	4.56	7618.2	−2.5
.44577	1.3032	3402.8	5.29	7621.5	+0.8
.47013	1.3747	3589.5	5.78	7622.7	+2.0
.47239	1.3810	3605.8	5.78	7620.9	+0.1
			Mean	7620.8	±1.2
		cis-4,4′-Dinitrostilbene			
1.04644	2.4919	6507.2	16.25	6202.9	+0.4
0.91376	2.1765	5683.2	14.04	6204.2	+1.8
.98420	2.3449	6123.0	19.87	6201.1	−1.4
.91790	2.1850	5705.6	13.25	6201.5	−0.9
.62492	1.4882	3885.8	10.58	6201.1	−1.3
.87834	2.0916	5461.5	12.48	6203.8	+1.4
			Mean	6202.4	±1.2
		trans-4,4′-Dinitrostilbene			
1.59261	3.7818	9876.1	24.96	6185.6	+0.5
0.83715	1.9890	5193.7	15.93	6185.0	− .1
.86506	2.0539	5363.0	12.45	6185.2	+ .1
.90206	2.1417	5592.6	13.11	8185.2	+ .1
1.03985	2.4696	6448.8	17.87	6184.5	− .6
0.82766	1.9655	5132.4	13.35	6184.9	− .2
.90526	2.1495	5613.0	13.28	6185.7	+ .6
			Mean	6185.2	±0.3

[a] Corrected for the heat of stirring and for the combustion of the iron wire.

Since no data are available for fusion or vaporization, calculations for the liquid or gaseous state are not feasible at present.

Results

The results are shown in Tables I and II. Due to the small amount of the 4-mononitrostilbenes available, the size of the sample burned was somewhat smaller than desirable and the precision obtainable was not as good as for the others.

TABLE II

THERMOCHEMICAL DATA FOR *cis*- AND *trans*-ISOMERS OF THE STILBENES AT 25° (DEFINED KILOCALORIES PER MOLE)

	4-Mononitrostilbene mol. wt. = 225.24 *cis*-	*trans*-
$-\Delta U_B$	1723.5 ± 0.2	1716.5 ± 0.2
$-\Delta U_R$	1722.5 ± .2	1715.5 ± .2
$-\Delta H_R$ (Combustion)	1723.2 ± .2	1716.2 ± .2
ΔH_f^0	30.73 ± .20	23.73 ± .20
Heat of isomerization *cis*- (solid) → *trans*- (solid).		$-\Delta H$ = 7.0 ± 0.4 kcal./mole.
	4,4′-Dinitrostilbene mol. wt. = 270.24 *cis*-	*trans*-
$-\Delta H_B$	1676.1 ± 0.1	1671.5 ± 0.04
$-\Delta U_R$	1675.6 ± .1	1671.0 ± .04
$-\Delta H_R$ (Combustion)	1675.3 ± .1	1670.7 ± .04
ΔH_f^0	17.00 ± .10	12.40 ± .04
Heat of isomerization *cis*- (solid) → *trans*- (solid).		$-\Delta H$ = 4.6 ± 0.3 kcal./mole.

Summary

There have been presented heats of combustion for two *cis–trans* pairs of nitro-substituted stilbenes, from which the energies of isomerization in the normal state have calculated.

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[4] Washburn, *J. Research Natl. Bur. Standards*, **10**, 544 (1933).