sis products which were found in the expected positions of glyceric acid and glycolic acid.[5]

The radioactive sugar was epimerized in pyridine.[6] Co-chromatography of the resultant mixture[7] with ribose and arabinose showed identity of the two major radioactive products with the added sugars. The radioactive 2,4-dinitrophenylosazone[8] of D-arabinose was prepared with a tracer quantity of the labeled ribulose. It was found to have the calculated specific activity and this was undiminished by repeated recrystallizations from methyl cellosolve.

The radioactive sugar was catalytically hydrogenated with Adams catalyst and the product was found to co-chromatograph with added ribitol but not with arabitol.

The foregoing observations lead to the conclusion that the radioactive compounds isolated from plants are ribulose 1,5-diphosphate and monophosphate. An examination of the kinetics of formation of this compound from $C^{14}O_2$ during steady state photosynthesis and a discussion of its importance as a C_2 donor in the cycle for regeneration of the CO_2-acceptors will be published.

[5] Phosphoglycolic acid observed as a minor radioactive product of $C^{14}O_2$ photosynthesis has been separated and identified. Oxidation during chromatography may provide one source of this phosphoglycolic acid.

[6] O. T. Schmidt and R. Treiber, *Ber.*, **66B**, 1765 (1933).

[7] The equilibrium mixture of epimers is known to be largely ribose and arabinose (P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, **102**, 563 (1933)). Small amounts of radioactive ribose observed in isolations of ribulose may indicate that it is also present in the original phosphate esters.

[8] C. Neuberg and E. Strauss, *Arch. Biochem.*, **11**, 457 (1946).

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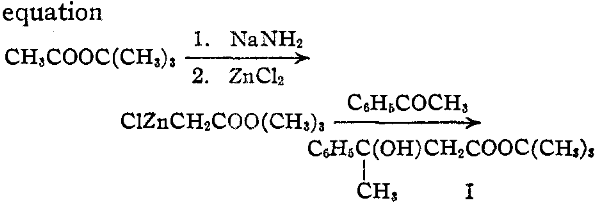
RECEIVED MAY 9, 1951

β-HYDROXY ESTERS FROM KETONES AND ESTERS

Sir:

We have simulated the Reformatsky type of reaction employing *t*-butyl acetate instead of an α-halo ester in accordance with the following equation



$$CH_3COOC(CH_3)_3 \xrightarrow[2.\ ZnCl_2]{1.\ NaNH_2} ClZnCH_2COO(CH_3)_3 \xrightarrow{C_6H_5COCH_3} \underset{\displaystyle CH_3}{C_6H_5C(OH)}CH_2COOC(CH_3)_3 \quad I$$

t-Butyl acetate was converted to its sodio derivative by means of sodium amide in liquid ammonia, the liquid ammonia replaced by ether, and an ether solution of anhydrous zinc chloride added at −70°. After stirring forty minutes at this temperature, acetophenone was added and the mixture refluxed two hours. There was obtained a 31% yield of *t*-butyl β-hydroxy-β-phenylbutyrate (I), b.p. 124–127° at 4.5 mm. *Anal.*[1] Calcd. for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 70.77; H, 8.22. Acid hydrolysis and dehydration yielded β-methylcinnamic acid, m.p. and mixed m.p. with an authentic sample, 97–98°.[2]

In a similar manner, *t*-butyl acetate condensed with cyclohexanone and benzaldehyde to form *t*-butyl 1-hydroxycyclohexylacetate (34% yield, b.p. 132–136° at 18 mm. *Anal.*[1] Calcd. for $C_{12}H_{22}O_3$: C, 67.35; H, 10.36. Found: C, 67.24; H, 10.02), and *t*-butyl β-hydroxy-β-phenylpropionate (58% yield, b.p. 154–158° at 10 mm. *Anal.*[1] Calcd. for $C_{13}H_{18}O_3$: C, 70.33; H, 8.17. Found: C, 69.98; H, 7.83), respectively.

We have further found that this type of aldol condensation may be effected more conveniently and in higher yield by means of lithium amide (without the use of zinc chloride).

$$CH_3COOC(CH_3)_3 \xrightarrow{LiNH_2} LiCH_2COOC(CH_3)_3 \xrightarrow{C_6H_5COCH_3} I$$

The lithium derivative of *t*-butyl acetate was prepared with lithium amide in liquid ammonia, the ammonia replaced by ether, and the acetophenone added immediately. After refluxing two hours, the hydroxy ester (I), b.p. 111–112.5° at 2 mm. was isolated in 76% yield.

This aldol condensation using lithium amide is particularly striking since use of sodium amide under similar conditions failed to give hydroxy ester.

These important types of aldol condensations are being investigated more thoroughly, employing various lithium and other metallic reagents. The results promise to be of both theoretical interest and of practical value.

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RECEIVED APRIL 24, 1951

[1] Analyses by Clark Microanalytical Laboratory, Urbana, Illinois.

[2] Rupe and Busolt, *Ber.*, **40**, 4538 (1907).

[3] Carbide and Carbon Chemicals Fellow.

THE HEAT OF DISSOCIATION OF NITROGEN*

Sir:

In recent publications[1,2,3,4] each of the four spectroscopically acceptable nitrogen dissociation energies, 7.383, 8.573, 9.764 and 11.8 ev. has been again recommended as the correct one. The study of stationary detonation waves provides information on equilibria at high temperatures because Zeldovitch[5] and v. Neumann[6] conclusively show on solid hydro-thermodynamic basis that the properties of an infinite plane wave without rarefaction are determined by the state of complete thermodynamic equilibrium of explosion products. The experimental problem consists largely in adducing the proof that a finite wave has the same velocity as the ideal one. We had been thus engaged to redetermine the heats of sublimation of carbon and of the dissociation of nitrogen when a paper by Döring and Schön appeared.[7] They compare the calculated

* This research was made possible by funds extended Harvard University under ONR Contracts M5ori-76 to XIX NR-053-094.

[1] L. Pauling, *Proc. Nat. Acad. Sci.*, **35**, 359 (1949).

[2] L. Brewer, L. K. Templeton and F. A. Jenkins, THIS JOURNAL, **73**, 1462 (1951).

[3] A. G. Gaydon, "Dissociation Energies," Chapman and Hall, London, 1947.

[4] G. Glockler, *J. Chem. Phys.*, **19**, 124 (1951).

[5] Ya. B. Zeldovich, *J. Exp. Theor. Phys.* (*USSR*), **10**, 542 (1950).

[6] J. v. Neumann, OSRD Report No. 549, May, 1942.

[7] W. Döring and G. Schön, *Z. Elektrochem.*, **54**, 231 (1950).

detonation velocity in equimolar cyanogen-oxygen mixtures with the measurements of Dixon.[8] Serious objections can be raised to those calculations and the measurements, but the finding that the dissociation energy is higher than 7.383 ev. is correct.

Our measurements, made with piezoelectric gates,[9] since improved, included tubes of 1.2 to 10 cm. diameter in 180 cm. lengths. No change of detonation velocity with the distance was apparent within the high precision of these measurements (±5 m./sec.), ruling out effects of rarefaction, which tends to *lower* detonation velocity. Figure 1 shows the effect of tube diameter and makes clear that infinite wave has been closely approximated.

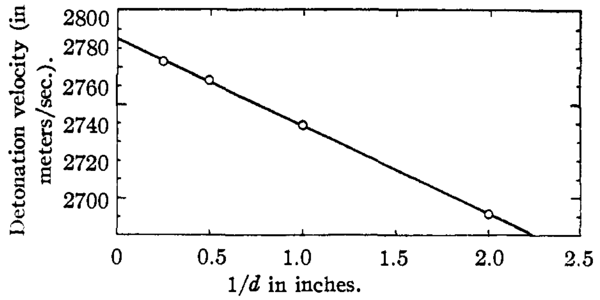

Fig. 1.—Detonation velocity plotted against the reciprocal of pipe diameter: 50% C_2N_2 + 50% O_2 at 1 atm. initial pressure.

Calculations of thermodynamic equilibria used the new heat of combustion of cyanogen[10] and Bureau of Standards Thermodynamic Tables, extrapolated by us to 5600–6400°K., the temperatures involved in the detonation of equimolar cyanogen-oxygen mixtures. We allowed for equilibria between CO, N_2, CN, C, N, O, since concentrations of NO, C_2N_2, O_2, C_2, CO_2 were shown by rougher calculations to be too low to affect the results significantly. The values in Fig. 2 are based on 170 kcal. for the sublimation heat of carbon and on 101 or alternately on 140 kcal. for the reaction $C_2N_2 \rightarrow 2\,CN$. Recent measurements[2] indicate an intermediate value. The velocity for 8.573 ev. has been interpolated on the curves and the slope of the upper curve is estimated from rougher calculations. Dotted lines give total error limits for the experimental value. Table I compares calculated and measured detonation velocities for three total pressures and for a mixture containing additional nitrogen.

TABLE I

OBSERVED AND CALCULATED DETONATION VELOCITIES

		%		%		%		%
Initial conditions	C_2N_2	49.9	C_2N_2	49.9	C_2N_2	49.9	C_2N_2	42.3
	O_2	49.9	O_2	49.9	O_2	49.9	O_2	42.3
	A	0.2	A	0.2	A	0.2	A	0.2
							N_2	15.2
	$P = 0.5$ atm.		$P = 1$ atm.		$P = 1.5$ atm.		$P = 1$ atm.	
V meas. meters/sec.	2745 ± 5		2773 ± 5		2780 ± 5		2678 ± 5	
V calcd. meters/sec.[a]	2742		2769		2780		2678	

[a] Using D_{N_2} = 225 kcal.; λ_0 = 170 kcal.; $C_2N_2 \rightarrow 2CN$ + 140 kcal.

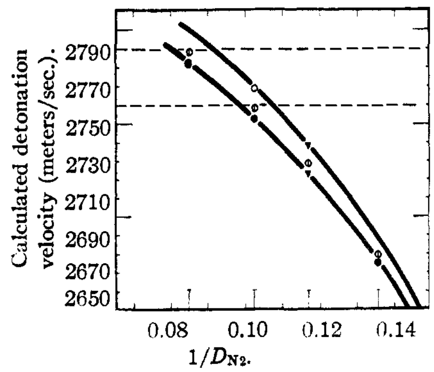

Fig. 2.—Comparison of calculated and measured detonation velocities: ○, calculated assuming $D_{C_2N_2}$ = 140 kcal.; ●, calculated assuming $D_{C_2N_2}$ = 101 kcal.; ▼, interpolated for D_{N_2} = 8.573 ev.; ⦶, interpolated taking $D_{C_2N_2}$ = 114 kcal.[2]; dotted lines indicate limits of experimental uncertainty.

These data eliminate the two lower values of the dissociation energy. A clear-cut decision between 9.764 and 11.8 ev. is not yet possible, but Herzberg[11] has adduced such strong evidence against the higher value that the 9.764 ev. (225 kcal.) value appears to be proven. The 170 kcal. for the sublimation energy of carbon[12] is indirectly supported by these data since the dissociation energy of nitrogen must be raised by a commensurate amount, if a lower figure is taken for carbon, to bring calculation and experiment into agreement again.

Further data pertinent to energies of nitrogen dissociation and sublimation of carbon will be published later.

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(8) H. B. Dixon, *Phil. Trans.*, **A184**, 97 (1894).

(9) D. J. Berets, E. F. Greene and G. B. Kistiakowsky, THIS JOURNAL, **72**, 1080 (1950).

(10) Private communication from Dr. E. J. Prosen of the Bureau of Standards.

(11) G. Herzberg, paper delivered before Am. Phys. Society Meeting, Pittsburgh, March, 1951.

(12) L. Brewer, P. W. Gilles and F. A. Jenkins, *J. Chem. Phys.*, **16**, 797 (1948).

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RECEIVED MAY 4, 1951

RESOLUTION INTO OPTICAL ISOMERS OF SOME AMINO ACIDS BY PAPER CHROMATOGRAPHY

Sir:

We have attempted to resolve several amino acids by means of paper chromatography, using *l*-methyl-(β-phenylisopropyl)-amine ([α]D −17.8°) as a solvent.

The results are shown in Fig. 1.

While the *d*- and *l*-forms of leucine gave the same R_f values (a), those of the acidic amino acids, glutamic acid (b), and tyrosine (c) gave differences in R_f values from 0.02 to 0.03. In the case of *d*- and *l*-isomers of tyrosine-3-sulfonic acid (d, e), the difference in R_f values was 0.21, and the racemic mixture was also completely resolved.

We had anticipated that the R_f values of *d*- and *l*-amino acids should be reversed when the *d*-solvent was used. However, identical results were observed using *d*-, *l*- and *dl*-solvents. The tendency to resolve was also observed when in-