

intermediate, *i.e.*, by way of the symmetric σ -bonded conjugate acid. This is virtually equivalent to asking whether the mechanism is actually IIb or is something nearer to IIa? When, as for the azulenes, the conjugate acid can itself be easily formed and studied, it is most plausible to assume its participation. Furthermore, as Melander^{6,7} has noted, similar stable intermediates are plausible participants in most electrophilic substitutions. The implication of reaction *via* the conjugate acid is illustrated semiquantitatively for azulene itself in Fig. 3. The position of the minimum for the intermediate can be determined since the pK of azulene is known to be -1.7 .¹⁶ This leads to ΔF° for the equilibrium protonation of roughly 2.5 kcal./mole. Since ΔF^* for the exchange reaction is 19 kcal./mole, the general shape of Fig. 3 is established.

An important implication of Fig. 3 is that the kinetics of formation of the conjugate acid species or of its decomposition should be predictable from data on the exchange reaction. For the particular case of azulene the predicted rates, under experimentally attainable conditions, are slow enough to be measurable. This suggests the possibility of directly verifying

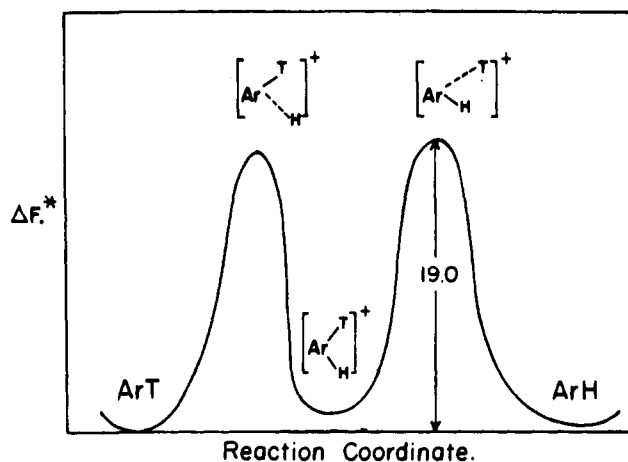


Fig. 3.—Free energy pattern of the acid-catalyzed detritiation reaction of azulene- $H^+(1)$.

that the exchange reaction does proceed *via* the conjugate acid intermediate and experiments along this line are now in progress.

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Strain Energies in Hydrocarbons from Heats of Combustion. II. Concerning the Possibility of a Transannular Interaction in 1,8-Cyclotetradecadiyne¹

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Heats of combustion of solid $C_{14}H_{28}$ and $C_{14}H_{20}$ and heats of sublimation from Knudsen effusion studies have been used to show that there is no appreciable transannular interaction in 1,8-cyclotetradecadiyne.

Some preliminary combustion calorimetric data led Wotiz and co-workers³ to suggest that an appreciable transannular interaction between the triple bonds was present in 1,8-cyclotetradecadiyne. These data actually yielded a negative heat of formation while one would predict about +70 kcal./mole for the heat of formation of the gas from normal bond energies. A more detailed study was undertaken to see if there was unequivocal evidence for strong transannular bonding in this molecule.

Experimental Results

Carefully purified samples of both the 1,8-cyclotetradecadiyne ($C_{14}H_{20}$) and its saturated analog cyclotetradecane ($C_{14}H_{28}$) were used in these high-precision measurements. Heats of oxidation were measured in the oxygen bomb calorimeter described by Frisch.⁴

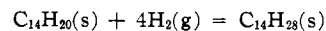
In Tables I and II are presented the heat of oxidation data for the solids $C_{14}H_{28}$ and $C_{14}H_{20}$. From four combustions of $C_{14}H_{28}$, a heat of formation of -88.94 ± 0.98 kcal./mole was obtained, in good agreement ($\pm 0.03\%$) with data on $C_{14}H_{28}$ reported by Coops, *et al.*⁵ For the alkyne, a heat of formation of $+35.31 \pm 0.56$ kcal./mole was obtained from five runs (Table II). Carbon was produced in several of the runs and cor-

rected for at the rate of 7.84 cal./mg. These data were derived using a density⁶ of 0.942 g./cc. for $C_{14}H_{28}$ and 1.040 g./cc. for $C_{14}H_{20}$ and the molecular weights of 196.379 and 188.316, respectively.

Vapor pressure measurements were made by the Knudsen technique on both $C_{14}H_{28}$ and $C_{14}H_{20}$ with the vacuum microbalance.⁷ A dewar flask thermostat was used for temperature control with a light bulb serving as a heater. The results are summarized in Tables III and IV. The two experiments for $C_{14}H_{28}$ were averaged, weighted by the reciprocal of their uncertainties, to yield $\Delta H_s = 32.21 \pm 0.35$ kcal./mole, from which the heat of formation for the gas was derived as -56.73 ± 0.76 kcal./mole. The single set of data on $C_{14}H_{20}$ gave $\Delta H_s = 39.68 \pm 0.76$ kcal./mole and the resulting heat of formation of the gas is $+74.99 \pm 0.95$ kcal./mole.

Discussion

The oxidation data yield the heats of formation of the solids; one derives, for the reaction



a heat of -124.25 ± 0.91 kcal./mole. With the heats of sublimation one finds the heat of hydrogenation in the vapor phase to be -131.72 ± 0.95 kcal./mole. Conn, Kistiakowsky, and Smith⁸ have determined the heat of hydrogenation of dimethylacetylene in the

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(7) (a) L. Dreger, V. Dadape, and J. Margrave, *J. Phys. Chem.*, **66**, 1556 (1962); (b) R. C. Paule, Ph.D. Thesis, University of Wisconsin, 1962.

(8) J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *J. Am. Chem. Soc.*, **61**, 1868 (1939).

(1) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

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(3) J. H. Wotiz, R. F. Adams, and C. G. Parsons, *J. Am. Chem. Soc.*, **83**, 373 (1961).

(4) M. A. Frisch, Ph.D. Thesis, University of Wisconsin, 1962.

(5) J. Coops, H. van Kamp, W. A. Lambregts, B. J. Visser, and H. Dekker, *Rec. trav. chim.*, **79**, 1226 (1960).

TABLE I
 HEAT OF COMBUSTION OF CYCLOTETRADECANE^a

Run	<i>m</i> (air), g.	ΔR , ohm	$-\Delta E_{\text{tot}}$, cal.	ΔE_{fuse} , cal.	ΔE_{ign} , cal.	$-\Delta E_c$, cal. g. ⁻¹	Deviation, cal. g. ⁻¹	
1	0.55906	0.0768922	6221.21	5.30	0.94	11116.84	0.83	
2	.55940	.0769732	6227.77	5.12	1.02	11121.96	5.95	
3	.55991	.0769773	6228.10	5.78	0.62	11111.96	-4.05	
4	.56129	.0771756	6244.14	5.37	0.99	11113.30	-2.72	
						Average	11116.02	± 2.23

$$\Delta E_c = -2180.58 \pm 0.88 \text{ kcal./mole}$$

$$\Delta E_c^\circ = -2180.04 \pm 0.88 \text{ kcal./mole}$$

$$\Delta H_c^\circ = -2184.19 \pm 0.88 \text{ kcal./mole}$$

$$\Delta H_f^\circ_{298.16} = -88.94 \pm 0.98 \text{ kcal./mole}$$

^a Coops, *et al.*,⁵ reported $\Delta H_c^\circ = -2183.48 \text{ kcal./mole}$.

 TABLE II
 HEAT OF COMBUSTION OF 1,8-CYCLOTETRADECADIYNE

Run	<i>m</i> (air), g.	ΔR , ohm	$-\Delta E_{\text{tot}}$, cal.	ΔE_{fuse} , cal.	ΔE_{ign} , cal.	ΔE_{carbon} , cal.	$-\Delta E_c$, cal. g. ⁻¹	Deviation, cal. g. ⁻¹
3	0.58298	0.0779333	6306.53	6.09	0.73	0	10806.03	0.22
4	.58126	.0777149	6288.85	6.13	.77	0	10807.48	1.67
5	.57975	.0774750	6269.44	6.17	.60	-0.71	10803.59	-2.22
6	.57778	.0772377	6250.24	6.05	.77	-.24	10806.29	0.48
7	.57772	.0772280	6249.45	6.36	.60	-.16	10805.67	-0.14
						Average	10805.82	± 0.64

$$\Delta E_c = -2032.93 \pm 0.40 \text{ kcal./mole}$$

$$\Delta E_c^\circ = -2032.22 \pm 0.40 \text{ kcal./mole}$$

$$\Delta H_c^\circ = -2035.18 \pm 0.40 \text{ kcal./mole}$$

$$\Delta H_f^\circ_{298.16} = +35.31 \pm 0.56 \text{ kcal./mole}$$

 TABLE III
 VAPOR PRESSURE DATA FOR C₁₄H₂₈

<i>T</i> , °K.	<i>P</i> , atm.	<i>T</i> , °K.	<i>P</i> , atm.
(a) Experiment 1		(b) Experiment 2	
295.5	1.34×10^{-5}	303.2	3.29×10^{-5}
294.7	1.31×10^{-5}	306.2	5.62×10^{-5}
303.1	6.62×10^{-5}	308.2	8.27×10^{-5}
309.0	1.84×10^{-4}	310.2	1.12×10^{-4}
313.0	2.96×10^{-4}	313.2	1.88×10^{-4}
		305.2	4.88×10^{-5}
		297.4	1.26×10^{-5}
		300.7	2.10×10^{-5}
		304.0	3.62×10^{-5}
		307.3	6.40×10^{-5}

 TABLE IV
 VAPOR PRESSURE DATA FOR C₁₄H₂₀

<i>T</i> , °K.	<i>P</i> , atm.	<i>T</i> , °K.	<i>P</i> , atm.
317.1	4.75×10^{-5}	324.3	2.07×10^{-4}
324.3	2.02×10^{-4}	328.1	4.25×10^{-4}
330.2	6.02×10^{-4}	332.4	8.51×10^{-4}

vapor at 82° as $-65.581 \pm 0.130 \text{ kcal./mole}$ which agrees well with the heat of hydrogenation per triple bond for C₁₄H₂₀(g) measured here ($-65.86 \pm 0.47 \text{ kcal./mole}$). These results do not indicate any significant energy anomaly in the behavior of the two triple bonds.

Dale, *et al.*,⁹ have recently determined the crystal structures of a series of diynes, including 1,8-cyclo-

(9) J. Dale, A. Hubert, and G. King, *J. Chem. Soc.*, 73, 86, 93 (1963).

tetradecadiyne, and also found no indication of an interaction in the solids. The triple bonds are $4.1 \pm 0.1 \text{ \AA}$ apart.

Finally, it is important to point out that, although bond energy calculations following Cottrell¹⁰ yield a consistent heat of hydrogenation based on a $\text{C}\equiv\text{C}$ bond energy of 203.2 kcal./mole derived from data on 2-yne, there is a discrepancy in the calculated standard heats of formation of gaseous C₁₄H₂₈ and C₁₄H₂₀ based on the $\text{C}\equiv\text{C}$ energy cited, a C—C bond energy of 82.6 kcal./mole and a C—H bond energy of 98.7 kcal./mole. Dale, *et al.*,⁹ have pointed out that cyclo-tetradecane has a majority of bonds in the gauche-orientation and that the diyne has gauche-bonds of the alkyl-ethynyl type. Therefore, small deviations from "standard" bond energies are to be expected. In addition, the heats of sublimation and vapor pressures are only upper and lower limits, respectively, if there is a low condensation coefficient involved in the sublimation process. The apparent entropy of sublimation is quite high. In any case, the difference between the heats of sublimation should be reliable. Further studies of this and similar sublimation processes for complex organic molecules are in progress.

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(10) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths Scientific Publications, London, 1958, pp. 152, 173, 242–243.