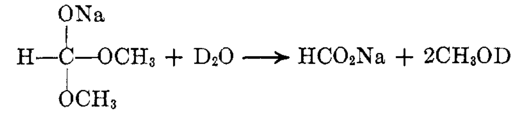
spectroscopy. This method suffers from none of the disadvantages found by earlier workers.[9,10]

A portion of the crude sodio methyl formylacetate was dissolved in heavy water and a portion dissolved in ordinary water. These samples were examined by nmr spectroscopy. The peaks (in Hertz) in heavy water were a, −237 (broad); b, −223; c, 0 (H_2O); d, 63; and e, 79. The peak labeled c was the trace of H_2O present and was used as the reference point. The ratio of a:d was 1:3, and that of b:e was 1:6. In ordinary water the same spectrum was obtained except that peak a became a doublet with a splitting of 11 Hz.

The peaks at b and e were shown to be due to formate anion and methanol, respectively. They resulted from the hydrolysis of the sodium methoxide–methyl formate adduct referred to earlier. To demonstrate this, we stirred a mixture of sodium methoxide and methyl formate in an autoclave under carbon monoxide pressure (to prevent decomposition of the methyl formate). The resulting paste was rapidly vacuum dried and dissolved in heavy water. Two peaks (besides the residual H_2O peak) were seen, corresponding in position to peaks b and e above, in the ratio of 1:6.



$$H\text{—}C(ONa)(OCH_3)\text{—}OCH_3 + D_2O \longrightarrow HCO_2Na + 2CH_3OD$$

The formyl hydrogen is assigned to peak a. The adjacent vinyl hydrogen exchanges with the solvent. When it is D, the peak at a is broad. In ordinary water, where it is H, it splits peak a by 11 Hz. The vinyl hydrogen in this latter case is obscured by the large water peak. Peak d is, of course, the methyl hydrogen of the ester, and the ratio of a:d of 1:3 is as is to be expected.

The ratio of a:b, or of d:e, then, affords an analysis of the mixture. It was about 75% sodio methyl formylacetate.

Interestingly, *no* evidence was seen for any sodio methyl acetoacetate which would be a likely impurity formed by the self-condensation of two molecules of methyl acetate in the presence of sodium methoxide.

Experimental Section

Methyl Trimesate.—A 300-ml stirred autoclave was charged with 10.2 g (0.189 mole) of sodium methoxide (Matheson Coleman and Bell) and 15.0 ml (0.189 mole) of methyl acetate (Matheson Coleman and Bell). The autoclave was rapidly sealed, pressurized with carbon monoxide (Matheson, CP grade), vented several times to purge air from the system, pressurized to 890 psig with carbon monoxide, and stirred at 1000 rpm overnight (about 16 hr). The thick, almost solid, residue was acidified with 20 ml of 10 *M* acetic acid and heated, with stirring, in a water bath at 50° for 3 hr. The buff ester was filtered and dried: 8.20 g, 51.7% yield, mp 137–140°. Recrystallization from methanol gave colorless material, mp 142–144°.

Nuclear magnetic resonance assay was performed with a Varian A-60 spectrometer. The heavy water used was 99.5 mole % D_2O minimum (Matheson Coleman and Bell). The crude sodio methyl formylacetate used was prepared as above and vacuum dried to remove volatile methyl formate.

Registry No.—Carbon monoxide, 630-08-0; methyl trimisate, 2672-58-4.

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The Enthalpy of Sublimation of Adamantane[1a]

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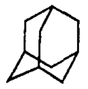
Adamantane (tricyclo[3.3.1.1.^{3,7}]decane, I) possesses a unique diamondoid structure which may be formally derived from the rigid fusion of three chair-form cyclohexane rings. A recent review on adamantane suggests that this geometry should result in an essentially strain-free molecule.[2] However, experimental verification for this hypothesis has been unavailable since no value for the enthalpy of sublimation has been reported. We have recently measured the sublimation pressure of adamantane between 40 and 80° and have calculated the enthalpy of sublimation from these data using the integrated form of the Clausius–Clapeyron equation. The data represent the arithmetic mean of three independent measurements on a dibutylphthalate manometer which agreed within 0.3 mm. The readings from the oil manometer were converted to Torrs by using 1.048 g/cm^3 as the density of the dibutylphthalate and 13.595 g/cm^3 as the density of mercury.



I

These data, by means of a least-squares fit, yield the following expression for the temperature dependence of

$$\log p = 9.40 - 3054.2/T$$

the sublimation of adamantane. Calculated standard deviations are

$$\log p = 0.01,\ \text{slope} = 31.3,\ \text{intercept} = 0.09$$

Although there are a number of assumptions involved in the use of the Clausius–Clapeyron equation to derive the enthalpy of sublimation from the above data, more rigorous calculations[3] require physical data which are not available. Estimation of the critical properties of adamantane in order to apply a reduced equation of state is precluded by its unusually high melting point, the lack of a reliable value for its normal boiling point,[2] and its unique structure. As a result, we have calculated the following value for the enthalpy of sublimation of adamantane at 333.2°K from the Clausius–Clapeyron equation with no correction for nonideality of the gas phase. (See Table I.) The standard

$$\Delta H_{\text{sub}} = 14.0\ \text{kcal/mole}$$

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[1] (a) Supported by the National Science Foundation, Grant No. GP-4329; (b) The Royal Institute of Technology, Stockholm, Sweden; (c) to whom correspondence should be addressed.

[2] R. Fort and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

[3] A. J. Gottschal and A. E. Korvezee, *Rec. Trav. Chim.*, **72**, 465 (1953).

TABLE I

EXPERIMENTAL DATA

Temp, °K	Pressure, torrs
313.2	0.43
318.2	0.65
323.2	0.86
328.2	1.25
333.2	1.76
338.2	2.30
343.2	3.18
348.2	4.17
353.2	5.57

deviation of the slope in the expression for the temperature dependence of the sublimation pressure indicates an uncertainty in the above value of 0.14 kcal/mole. The possible error arising from the nonideal nature of the gas phase leads us to estimate an over-all error of 0.2 kcal/mole in the value we have reported for the enthalpy of sublimation of adamantane.

Comparison of this value with reported values for related molecules serves as a qualitative check on its validity. Bondi has recently summarized the published data on the enthalpy of sublimation of a large number of organic compounds, evaluated at the first transition point for the low-temperature form.[4] To compare our value with those reported by Bondi, it is necessary to reduce our figure to the first transition temperature of adamantane, reported by Chang and Westrum as 208.6°K.[5] To carry out this correction we used

$$\Delta H_{\text{sub}}^{208.6^\circ\text{K}} = \Delta H_{\text{sub}}^{333.2^\circ\text{K}} + \int_{208.6}^{333.2} c_{\text{p}}(s)\text{d}T - \int_{208.6}^{333.2} c_p(g)\text{d}T + \Delta H_{\text{tr}}^{208.6^\circ}$$

The heat capacity of solid adamantane and its enthalpy of transition have been reported by Chang and Westrum.[5] Its heat capacity in the gas phase may be estimated by the methods of Stull and Mayfield[6] and of Souders, *et al.*[7] Graphical integration furnishes a value of 0.09 kcal/mole for the term

$$\int_{208.6}^{333.2} c_{\text{p}}(s)\text{d}T - \int_{208.6}^{333.2} c_{\text{p}}(g)\text{d}T$$

while Chang and Westrum[5] report a value of 0.8 kcal/mole for ΔH_{tr} at 208.6°K. Combination of these figures with our value for $\Delta H_{\text{sub}}^{333.2^\circ\text{K}}$ results in a value of 14.9 kcal/mole for $\Delta H_{\text{sub}}^{208.6^\circ\text{K}}$.[8] This figure gives for adamantane a value of 0.93 kcal/mole for the enthalpy of sublimation per hydrogen atom, $\Delta H_{\text{s}}/H$, which agrees very closely with Bondi's calculated value for cyclohexane,[4] $\Delta H_{\text{s}}/H = 0.928$ kcal/mole, suggesting that the intermolecular interactions of the cyclohexane rings in adamantane are of the same magnitude as in solid cyclohexane itself. Bondi estimates the contribution of one CH or CH_2 group to the enthalpy of sublimation of an organic cage molecule at 1.45 kcal/mole from data on polar organic cage compounds. Our value for the enthalpy of sublimation of adamantane yields 1.49 kcal/mole for this figure, in rather good agreement with Bondi's value considering the approximate nature of his calculations.

In order to obtain a good estimate for the strain energy of adamantane, it is necessary to use an accurate value for the enthalpy of formation of the solid compound. The figure quoted in the recent review[2] is a private communication of Wineman, based on unpublished combustion data. Since we are unable to furnish a more reliable value, we have used Wineman's value, $\Delta H_f(s) = -47.0$ kcal/mole, together with our value for the enthalpy of sublimation to calculate the gas phase enthalpy of formation: $\Delta H_f(g) = -33.0$ kcal/mole.

Skinner and Pilcher[9] have summarized several schemes for estimating the enthalpy of atomization of hydrocarbons by empirical methods. Comparison of the values estimated by these methods with that obtained from the gas phase enthalpy of atomization of carbon and hydrogen gives a direct measure of the strain energy. We have applied the Allen–Skinner,[10] Laidler,[11] and Tatevskii[12] schemes to adamantane to calculate the enthalpy of atomization. Our experimental value was calculated from the above value for $\Delta H_f(g)$ together with values tabulated by Skinner and Pilcher[9] for the enthalpies of atomization of carbon and hydrogen.

It is evident from the figures in Table II that adamantane possesses a small strain energy.[13] The negative value obtained from the Tatevskii scheme has no physical significance, but rather reflects the occasional inadequacy of the estimation schemes for predicting absolute values of the enthalpy of atomization of complicated molecules.

TABLE II

HEATS OF ATOMIZATION AND STRAIN ENERGIES

	Experimental	Allen–Skinner	Tatevskii	Laidler
ΔH_{a}	2575.6 (2583.4)[a]	2578.96	2573.52	2583.8
Strain energy	...	3.3	−2.1	0.4

[a] Value obtained using values quoted by Laidler for enthalpies of atomization of the elements.

Experimental Section

The hydrocarbon (I) was prepared according to the literature procedure.[14] Four sublimations were carried out to ensure high purity. No impurity peaks could be detected by gas–liquid partition chromatography or infrared in the final product.

The sublimation pressure measurements were carried out with a high-sensitivity, double-spoon, pressure gauge developed by Monchamp, Bannister, and Cotton,[15] which was constructed according to the description of Cotton and Monchamp.[16] The sensitivity of the gauge, defined as the ratio of pointer deflection (millimeters) to pressure differential (millimeters of Hg), was approximately 3.

The adamantane was sublimed under high vacuum into a break-seal sample chamber which was then sealed off and connected to the apparatus as described by Cotton and Monchamp. The pressure gauge was evacuated overnight and then degassed

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(4) A. Bondi, *J. Chem. Eng. Data*, **8**, 371 (1963).

(5) S. S. Chang and E. F. Westrum, Jr., *J. Phys. Chem.*, **64**, 1547 (1960).

(6) D. D. Stull and F. D. Mayfield, *Ind. Eng. Chem.*, **35**, 639 (1943).

(7) M. Souders, Jr., C. W. Mathews, and C. O. Hurd, *ibid.*, **41**, 1037 (1949).

(8) Professor E. F. Westrum Jr., has informed us that this value and our value for the enthalpy of formation of adamantane are substantially in agreement with those he has determined.

(9) H. A. Skinner and G. Pilcher, *Quart. Rev.* (London), **17**, 264 (1963).

(10) H. A. Skinner, *J. Chem. Soc.*, 4396 (1962).

(11) K. J. Laidler, *Can. J. Chem.*, **34**, 626 (1956).

(12) V. M. Tatevskii, *et al.*, "Rules and Methods for Calculating the Physico-Chemical Properties of Paraffin Hydrocarbons," Pergamon Press Ltd., London, 1961.

(13) Professor P. von R. Schleyer has informed us that he has analyzed the available thermochemical data on adamantane and has concluded that the molecule contains some 5 kcal of strain energy.

(14) P. von R. Schleyer, M. M. Donaldson, R. D. Nicholas, and C. A. Cupas, *Org. Syn.*, **42**, 8 (1961).

(15) R. R. Monchamp, E. Bannister, and F. A. Cotton, *Rev. Sci. Inst.*, **30**, 945 (1959).

(16) F. A. Cotton and R. R. Monchamp, *J. Chem. Soc.*, 533 (1960).

by heating with an infrared lamp for several hours while maintaining a high vacuum. This degassing procedure was adopted after several experiments showed evidence for the evolution of gases from the glass, even at the relatively low temperatures employed in this measurement. The sample break seal was then opened and evacuation was continued for several minutes to removes any gases desorbed from the sample chamber itself. The sample chamber was then cooled in liquid nitrogen, and the sample arm of the apparatus was sealed off.

Pressure measurements were carried out by carefully admitting air to the gauge envelope until the pointer returned to its 0 point as read by a wall-mounted telescope fitted with a scaled reticule. The balancing pressure was then read from a dibutylphthalate manometer using a cathetometer graduated to 0.05 mm. The vacuum are of the manometer was maintained at less than 0.1 μ by continuous pumping. The pressure gauge was immersed in a thermostat bath regulated to 0.5° by a bimetallic regulator. The temperature deviations actually observed during a pressure reading did not exceed 0.1°.

Registry No.—I, 281-23-2.

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Reduction of Nitrobenzene with Crabon Monoxide and Copper Salt–Amine Complexes

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Copper compounds are known to be effective in activating hydrogen in homogeneous solution[2] and carbon monoxide has recently been reported to reduce aromatic nitro compounds to the corresponding azo derivatives using iron pentacarbonyl as catalyst.[3] The author wishes to report that copper salt–amine complexes in conjunction with carbon monoxide can be used for the reduction of aromatic nitro compounds to the corresponding amines.

Cupric salts dissolve readily in an aqueous solution of ammonia or a variety of primary amines[4] to give deep blue solutions which are reduced to the corresponding cuprous compound or to metallic copper by carbon monoxide in the absence of oxidizing agents. The work now reported shows that if nitrobenzene, or other easily reducible nitro compound, is present it is reduced to the amine, usually in quantitative yield. This technique is, therefore, a convenient laboratory method for the selective reduction of nitro groups, especially in compounds containing other reducible groups such as double bonds or carbonyl groups. If the carbon monoxide is replaced by hydrogen the reaction is too slow to be of preparative value.

The pH of the copper salt–amine solution should be greater than 10 and the rate of reaction increases significantly as the pH is increased. In order to obtain high reaction rates the copper should be added as the hydroxide or as a salt of a weak acid and the amine should be highly basic and present in high concentration. Inasmuch as the amine reacts with the carbon dioxide formed in the reaction it is necessary to use an excess or, as an alternative, add sufficient sodium hydroxide to combine with the carbon dioxide. Tables I–III illustrate the effect of the variables on the rate of reduction of nitrobenzene to aniline at partial conversions. Complete conversions are readily obtained at conditions described in the Experimental Section.

Table I

Effectiveness of Amines on Nitrobenzene Reduction Rate

Amine[a]	Hr	Aniline yield, %
Ethylenediamine	5	50
1,2-Propanediamine	8	20
1,3-Propanediamine	7	Trace
3,3′-Diaminodipropylamine	5	85
1,6-Hexanediamine	7	11
Triethylenetetramine	5	16
Ammonia[b]	6	33

[a] Aqueous amine (50 ml of 50%) containing 2% by weight of copper acetate and 2 ml of nitrobenzene were used in these tests. See Experimental Section. [b] The ammonia was blended 1:1 with carbon monoxide and fed to the reactants in a Parr shaker at 2 atm of pressure.

Table II

Effect of Copper Concentration on Reduction Rate

Copper acetate concn[a]	Hr	Aniline, %
0.0	5	None
0.4	5	Trace
1.2	7	3
4.0	3	33

[a] Weight per cent in 10% aqueous ethylenediamine at 85°, conducted as in Table I.

Table III

Effect of Ethylenediamine Concentration on Reduction Rate[a]

Ethylenediamine, wt %	Hr	Aniline, %
1.4	6	Trace
4.0	6	10
10	6	20
50	5	50
90	6	90

[a] Containing 2 wt % of copper acetate.

The reducibility of a compound by this technique can be readily ascertained by passing carbon monoxide through the copper salt–amine solution until the reduction of cupric to cuprous is complete as indicated by disappearance of the deep blue color and then adding a drop of the compound to be reduced. A return of the deep blue cupric complex indicates reduction of the compound in question has occurred. Completion of the reduction can be determined by periodic gas–liquid partition chromatography (glpc) analysis or by passing carbon monoxide until the blue color characteristic of copper(II) has disappeared.

Nitromethane, *o*-nitroanisole, *o*-chloronitrobenzene, *p*-nitrobenzoic acid, and cumene hydroperoxide were all

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(1) Bureau of Mines, Pittsburgh, Pa. 15213.

(2) J. Halpern, in Proceeding of the 3rd International Congress on Catalysis, John Wiley and Sons, Inc., 1965, p 146; *Advan. Catalysis*, **9**, 302 (1957).

(3) J. E. Kmiecik, *J. Org. Chem.*, **30**, 2014 (1965).

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