transfer to polymer occurs to a slight extent. Copolymerization parameters show that the bicyclobutanes are equally reactive to vinyl monomers in copolymerization, the reactivities all falling within a factor of 10 of each other and of the corresponding vinyl monomers. This demonstrates that these compounds constitute a new class of reactive monomer.

Experimental Section

Values for reactivity ratios in the literature vary from author to author, and corrections of analytical data are routinely made. Carbon, hydrogen, nitrogen, and oxygen percentages did not always add up to 100%. (Triplicate Dumas determinations required least sample and gave the most consistent results for N.) In such cases the per cent of each element found was then increased proportionately until the sum was 100%. As a check, styrene–acrylonitrile in DMSO gave results in good agreement with literature values:[9] $r_{\text{styrene}} = 0.31$ (0.37) and $r_{\text{AN}} = 0.13$ (0.07). Our reactivity ratios are of the same quality as those found in the literature.

The equation of Fineman and Ross[4] was used as

$$\left(\frac{f_{\text{V}}}{f_{\text{V}}}\right)\left(\frac{F_{\text{V}} - F_{\text{B}}}{F_{\text{V}}}\right) = \left(\frac{f_{\text{V}}}{f_{\text{B}}}\right)^2\left(\frac{F_{\text{B}}}{F_{\text{V}}}\right)(r_{\text{V}} - r_{\text{B}})$$

where f_{V} = feed mole fraction of vinyl monomer and F_{V} = mole fraction of vinyl monomer in the resulting copolymer and correspondingly for the bicyclobutanes. Uncertainties in the intercept ($-r_{\text{B}}$) and the slope (r_{V}) should be about ±5%. Where comparison was made, homogeneous polymerizations gave the same reactivity ratios as polymerizations which became heterogeneous. In a typical run carrried to 1.5–3.6% conversion, AIBN, 0.0061 *M*, was the initiator in DMSO at 50° for 2 hr. These data are plotted in Figure 1. Similar data for the copolymerization of acrylonitrile with bicyclobutane-1-carbonitrile (1.5–2.5 hr; conversion 1.5–4.5%) are plotted in Figure 2.

Table VII

Sample	In feed Mol of Sty	Mol of BBC	f_{Sty}	In copolymer % N	Wt % Sty	F_{Sty}
A	0.01817	0.00771	0.702	2.88	83.74	0.796
B	0.01056	0.01403	0.429	5.57	68.55	0.623
C	0.01239	0.02111	0.370	6.21	64.94	0.586
D	0.00634	0.01707	0.271	7.44	57.99	0.512

The gel permeation chromatography experiments were done on 0.25% (w/v) solutions of the polymers in *N*-methylpyrrolidone on a series of 5 × 10⁶, 10⁵, and 10³ Å Styragel (cross-linked polystyrene) columns in a Waters Associates instrument at column temperatures of 90° and differential refractometer detector temperature at 75°.

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(9) H. Mark, B. Immergut, E. H. Immergut, L. J. Young, and K. I. Benynon, "Polymer Handbook," ref 7, pp II-144–II-155.

Thermochemistry of Strained-Ring Bridgehead Nitriles and Esters

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Contribution No. 1631 from the Central Research Department,
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Abstract: Enthalpies of formation of a variety of potentially polymerizable bicyclic bridgehead nitriles and esters were determined. Because plots of these enthalpies of formation against those for the corresponding hydrocarbon were linear with unit slope, specific stabilizations or destabilizations were minor. Replacement of H by CN in an organic molecule made $\Delta H_{f,g}{}^{\circ}{}_{298}$ more positive by 24 kcal mol^{-1}; by $COOCH_3$, more negative by 89 kcal mol^{-1}. An alternative derivation of the Flory equation, which relates enthalpies of hydrogenation to those of polymerization, is given. Using this alternative approach, enthalpies of polymerization were calculated for various strained ring systems. These agreed well with the calculated release of strain energy and lay in the order: bicyclo[2.2.0]pentanes > bicyclobutanes > bicyclo[3.1.0]hexanes > ethylenes.

Studies of the polymerization of substituted small strained carbocyclic rings showed that monomers containing bridgehead cyano and ester substituents polymerized most satisfactorily.[2,3] We have determined $\Delta H_{f,g}{}^{\circ}{}_{298^{\circ}}$, the standard enthalpies of formation, for various small-ring nitriles and esters to calculate the thermodynamics of their polymerization and place ring-opening polymerization of a strained C—C single bond on a quantitative basis.

Results

Enthalpies of combustion were determined with a precision Bureau of Mines type rotating bomb calorimeter. From them and the corresponding enthalpies of vaporization, enthalpies of formation in the gas phase at 298°K have been calculated. The results are given in Table I. We redetermined the enthalpies of formation of a few compounds for which data were already in the literature to check our technique; agreement was generally good. Precision was usually ±0.04%.

Correlation with Data for Corresponding Hydrocarbons. Table II summarizes the enthalpies of formation of the nitriles and the corresponding hydrocarbons, and Figure 1 plots these quantities against each other. The plot is linear, with the expected unit slope, and shows that replacement of H by CN in a simple organic molecule raises $\Delta H_{f,g}{}^{\circ}{}_{298}$ by +24 kcal mol^{-1}. This is consistent with the value of +27.5 kcal mol^{-1} recently found by Koniek, Prochazka,

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(1) Address correspondence to this author.

(2) H. K. Hall, Jr., E. P. Blanchard, Jr., S. C. Cherkofsky, J. B. Sieja, and W. A. Sheppard, *J. Amer. Chem. Soc.*, 93, 0000 (1971).

(3) H. K. Hall, Jr., C. D. Smith, E. P. Blanchard, Jr., S. C. Cherkofsky, and J. B. Sieja, *ibid.*, 93, 121 (1971).

Table I. Heats of Formation and Vaporization

Compound	C_p, J deg^{-1} g^{-1}	No. of expt	ΔU_c°	$\Delta H_{c,l}^\circ$	$\Delta H_{f,l}^\circ$	ΔH_{vap}°	$\Delta H_{f,g}^\circ$
Cyclopropanecarbonitrile	1.72	3	−580.21 ±0.17	−580.65	+33.65	+9.52	+43.17 +43.5[a]
Bicyclobutane-1-carbonitrile	1.67	6	−702.46 ±0.28	−702.90	+61.85	+10.93	+72.78
Cyclobutanecarbonitrile	1.80	3	−733.24 ±0.27	−733.98	+24.61	+9.57	+34.18
3-Methylenecyclobutane-carbonitrile	2.05	3	−852.36 ±0.49	−853.10	49.68	10.65	+60.33
Bicyclo[2.1.0]pentane-1-carbonitrile	1.76	3	−857.11 ±0.25	−857.85	54.42	10.60	65.02
Cyclopentanecarbonitrile	1.76	3	−870.86 ±0.24	−871.90	+0.16	9.82	9.98
Bicyclo[3.1.0]hexane-1-carbonitrile	1.59	4	−988.28 ±0.41	−989.31	23.52	10.43	33.95
Cyclohexanecarbonitrile	1.63	3	−1021.50 ±0.12	−1022.82	−11.28	10.42	−0.85
Acetonitrile	2.01	3	−297.93 ±1.71	−298.08	7.50 +12.69[b]	8.24 +7.83[b]	15.74 +20.52[b] +19.1[c]
Propionitrile	2.05	3	−456.21 ±0.13 −456.25[b]	−456.65	3.70 +3.30[b]	+8.60 +7.41	+12.30 +11.21[b] +12.4[a]
Isobutyronitrile	2.26	5	−611.27 ±0.31	−612.01 −612.40[b] −613.93[c]	−3.31 −2.92[b]	8.76	5.44 +5.6[b] +7.45
Pivalonitrile	1.84	3	−767.12 +0.17	−768.15	−9.53	8.76	−0.79 +5.62[a]
Acrylonitrile	2.01	3	−419.66 ±0.10	−419.79 −420.40[b] −420.8[d]	35.16 −35.75[b]	+7.8[b] +7.8[d]	42.95 +43.6[b] +43.7[a] +44.0[d]
Methyl bicyclobutane-1-carboxylate	1.72	3	−788.43 ±0.12	−789.02	−48.56	9.22	−39.34
Methyl cyclobutanecarboxylate	1.67	3	−810.58 ±0.31	−811.47	−94.42	9.50	−84.93
Methyl formate	1.59	2	−232.46 ±0.14	−232.46	−92.28	7.31 6.67[b]	−84.97 −81.0[a] −83.60[b]
Methyl acetate	1.67	2	−380.24 ±0.16	−380.54 −381.21[b]	−106.57 ±105.90[b]	8.57 +7.49[b]	−98.00 −98.43[b]
Methyl pivalate	1.92	2	−846.34 ±0.28	−847.52	−126.69 −131.93[b]	8.53	−118.16
Methyl acrylate	1.55	2	−494.29 ±0.16	−494.59	−86.57	6.98	−79.59
Methyl benzoate	1.59	2	−942.98 ±0.57	−943.57 −943.81[b]	−82.11 −81.88[b]	+10.45	−71.66 −71.74

[a] S. W. Benson, F. R. Cruikshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, T. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). [b] W. Auer in "Calorimetric Quantities," Landolt-Boernstein, Ed., Part 4, Springer-Verlag, Berlin, 1961, pp 349–354. [c] F. W. Evans and H. A. Skinner, *Trans. Faraday Soc.*, **55**, 255 (1959). [d] "The Chemistry of Acrylonitrile," 2nd ed, American Cyanamide Co., New York, N. Y., 1959, pp 9–10.

Krestanova, and Smisek,[4] and supplants the earlier value of +34.[5] The linearity seems reasonable because of the low steric requirements of CN: $\Delta G^\circ = -0.2$ kcal mol^{-1} as the preference for the CN group in equatorial over axial position.[6] The deviation for bicyclobutane-1-carbonitrile points to appreciable stabilization in this compound. The only other significant deviation is observed where R = CH_3; either acetonitrile is slightly destabilized or methane is slightly stabilized.

Table II also gives ΔH_f° values for the corresponding methyl esters. Values for several acyclic esters were determined to provide additional data for correlation. Figure 2 plots these results against the data for the corresponding hydrocarbons. Again a linear correlation is observed. The greater scatter, believed to be real, may be caused by a larger conformational preference for the $-COOCH_3$ group: $\Delta G^\circ = -1.1$ kcal mol^{-1} as the preference for equatorial over axial. A slightly different type of correlation has been given by Sunner and coworkers.[7]

Calculated Enthalpies of Polymerization. Flory[8] proposed the following relationship between the enthalpies of hydrogenation and of polymerization of

$$\Delta H_p = \Delta H_h + \Delta H_e$$

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(4) J. Konicek, M. Prochazka, V. Krestanova, and M. Smisek, *Collect. Czech. Chem. Commun.*, **34**, 2249 (1969).

(5) J. W. Anderson, G. H. Beyer, and K. M. Watson, *Nat. Petrol. News, Tech. Sect.* **36**, R476 (1944).

(6) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, pp 441–442.

(7) (a) B. Borjesson, Y. Nakase, and S. Sunner, *Acta Chem. Scand.*, **20**, 803 (1966); (b) M. Mansson, Y. Nakase, and S. Sunner, *ibid.*, **22**, 171 (1968).

(8) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., pp 249–250.

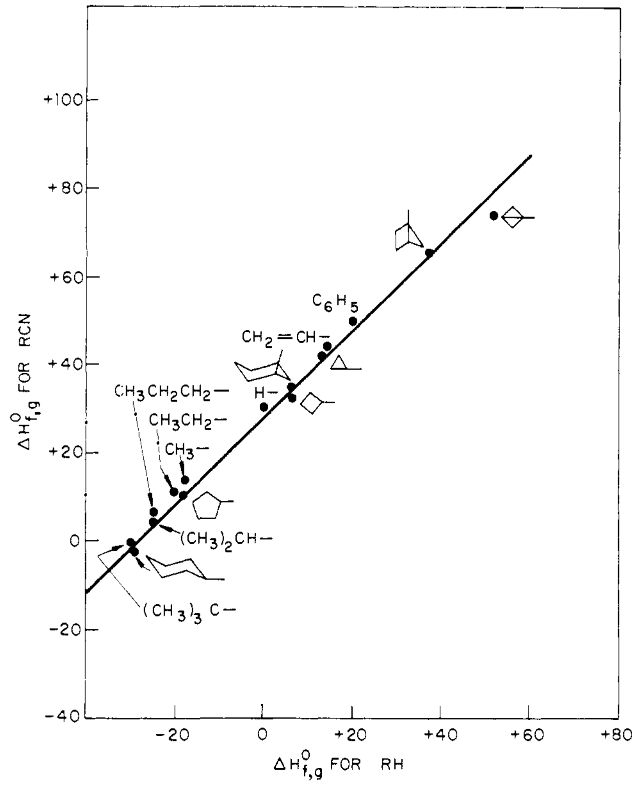


Figure 1.

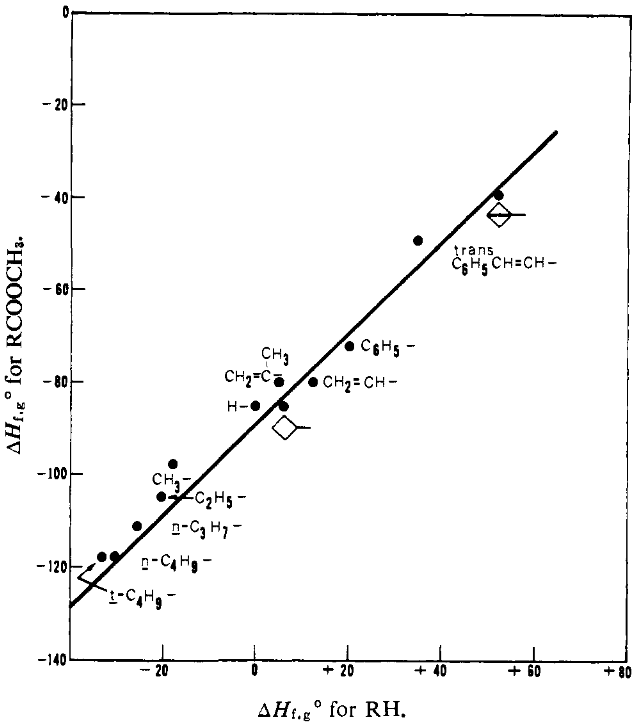
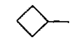
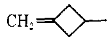
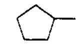


Figure 2.

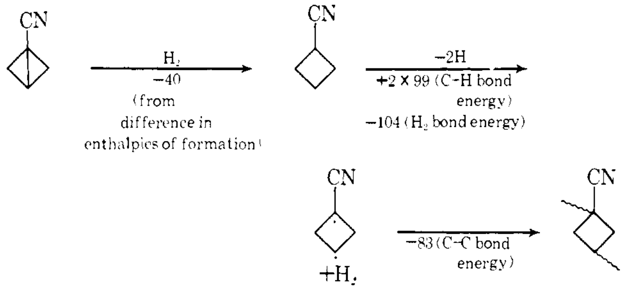
vinyl monomers where ΔH_e was ~10 kcal mol^{-1}. His equation was derived by extrapolating enthalpies of formation of hydrocarbons and combining them with enthalpies of isomerization. Practically the same equation can be derived from bond energies. When

Table II. Thermochemical Values for Strained Rings

	$\Delta H_{f,g}°_{298}$			Strain			
Radical	Nitrile, RCN	Methyl ester, $RCOOCH_3$	Hydrocarbon, RH^a	energy SE^g	$\Delta H_h{}^g$	$\Delta H_p{}^g$	$\Delta SE_p{}^g$
	43.2		12.7	28^e	−38	-27^d	−28
	72.8	−39.3	51.9	64^f	-46^c	−35	−38
	34.2	−84.9	6.4	26^e	−37	-26^d	−26
	60.3		30.0				
	65.0		37.6	54^f	−56	−45	−47
	10.0		−18.5	7^e	−17	-6^d	−7
	34.0		9.1	31^f	−39	−28	−31
	−0.9		−29.4	0^e	−11	0^d	0
H-	32.3^a	−85.0	0				
CH_3	15.7	−98.0	−17.9				
C_2H_5-	12.3	-105.1^b	−20.2				
n-C_3H_7-	7.5^a	-111.2^b	−24.8				
i-C_3H_7-	5.4		−24.8				
n-C_4H_9-		-117.8^b	−30.2				
tert-C_4H_9-	−0.8	−118.2	−32.2				
$CH_2=CH-$	43.0	−79.6	12.5	22	−33	−22	−22
$CH_2=C(CH_3)$		-79.3^a	4.9	22	−30	−19	−22
C_6H_5-	52.3^a	−71.7	19.8				
$C_6H_5CH=CH$ (*trans*)		−49.3	35.2				

[a] See Table I, footnote *a*. [b] See Table I, footnote *b*. [c] −40.6 by direct hydrogenation (R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968)). [d] Reference 9. [e] E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 93. [f] K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 191 (1969). [g] For hydrocarbons.

this approach is taken, the equation can be seen to apply to polymerization through strained C–C single bonds. For example



$$\Delta H_p = \Delta H_H + (2 \times 99) - 104 - 83$$

$$\Delta H_p = \Delta H_H + 11$$

(kcal mol^{-1}; all compounds in gas phase)

The quantity +11 kcal mol^{-1}, consists only of C–C and C–H bond energies and is the same for all monomers to this crude approximation. It could be refined if desired by considering whether the carbons are primary, secondary, or tertiary, and the nonbonded interactions among adjacent monomer units.

ΔH_p values of the various ring systems of interest to us were calculated and are listed in Table II. Because of the essentially linear relationships in ΔH (Figures 1 and 2), the values of ΔH_p will be the same for the hydrocarbon, nitrile, or ester. In practice, though, the presence of the latter groups provides a kinetically feasible route to equilibrium through either radical or anionic initiation.

Strain energies provide an alternate approach to polymerizability. As shown by Sunner and his colleagues,[7] the difference in strain energy between monomer and polymer equals the enthalpies of polymerization.[9] Table II lists the strain energies of mono- and bicyclic rings and the change in strain energy on polymerization. They agree well with the calculated ΔH_p values.

As already noted by Dainton and Ivin,[10] the monocyclic rings of 3–5 atoms are all unstable and should polymerize. No mechanism is yet available to accomplish this. The bicyclic compounds are also unstable, and in fact, have greater thermodynamic tendency to polymerize than ethylene. They fall in the following series: bicyclo[2.1.0]pentane > bicyclobutane > bicyclo[3.1.0]hexane > ethylene. Polymerization of members of the bicyclo[2.1.0]pentanes,[11] bicyclobutanes,[2,3] and ethylenes have been demonstrated so far.

Conclusions

The heats of formation of a variety of strained bicyclic nitriles and esters have been measured. Correlation with the heats of formation of the corresponding hydrocarbons shows (a) the data are internally consistent; (b) replacement of H by CN makes $\Delta H_f°$ more positive by 24 kcal mol^{-1} and by $COOCH_3$ more negative by about −89 kcal mol^{-1}; (c) heats of polymerization estimated by the Flory relationship and by calculation of strain energies agree; (d) the data agree with literature estimates of strain energies for the corresponding hydrocarbons; no large interactions of nitrile or ester with the rings are involved, except for bicyclobutane-1-carbonitrile; (e) the thermodynamic driving force for polymerization is bicyclo[2.1.0]pentanes > bicyclobutanes > bicyclo[3.1.0]hexanes > ethylenes.

Experimental Section

Compounds. Acetonitrile, propionitrile, isobutyronitrile, methyl formate, methyl acetate, and methyl benzoate were the best Eastman Kodak Co. grades, dried over Molecular Sieves and, except for acetonitrile, fractionally distilled in a 1 × 75 cm glass helix-filled column. Pivalonitrile, cyclopropanecarbonitrile, and cyclobutanecarbonitrile (Ash Stevenes Co.) were distilled similarly. Acrylonitrile was a polymerization-grade du Pont chemical, used as received. Methyl acrylate was a commercial polymerization-grade monomer and was redistilled before use. Cyclopentanecarbonitrile was prepared by reaction of bromocyclopentane with sodium cyanide in DMSO. Pivalic acid was crystallized from pentane and esterified with 2,2-dimethoxypropane, catalyzed by methanesulfonic acid. Cyclohexanecarbonitrile was prepared by hydrogenation of 3-cyclohexenecarbonitrile. Methyl cyclobutanecarboxylate was prepared by acid-catalyzed esterification of cyclobutanecarboxylic acid with 2,2-dimethoxypropane. 3-Methylenecyclobutanecarbonitrile,[2] bicyclobutane-1-carbonitrile,[2] bicyclo[2.1.0]pentane-1-carbonitrile,[11] bicyclo[3.1.0]hexane-1-carbonitrile,[11] and methyl bicyclobutane-1-carboxylate[3] were available from our research in this area. Except for the bicyclobutanes, which were quite pure as made, they were carefully redistilled before use.

All samples were >99.9% pure by gas chromatography on silicone gum nitrile or butanediol succinate columns. The esters were readily purified by careful fractional distillation. The original nitriles were often contaminated by trace impurities, which were removed by treatment with aqueous permanganate and/or distillation from P_2O_5, followed by repurification.

Calorimetry Equipment. The calorimeter was constructed according to the U. S. Bureau of Mines drawings 63-01 through 63-31. The bomb was Parr Model 1004-C which is interchangeable with the U. S. Bureau of Mines bomb. The bomb had an internal volume of 342 ml and its internal fittings and linings were of platinum. The specimen to be burned was placed in a platinum crucible which was supported by gimbols in the bomb. The bucket was chrome plated and its shape was exactly the same as the cavity in the isothermal jacket except that it was $^3/_8$ in. smaller in overall dimensions. A hollow cover fitted over the cavity.

The jacket temperature of the circulating H_2O was controlled by a Hallikainen "Thermotrol" unit at 25 ± 0.001°. The complete system was housed in a room kept at 23.0 ± 0.03°. The temperature of the water in the calorimeter and the bucket were measured by Leeds and Northup platinum resistance thermometers of the totally enclosed, necked sheathed type (Model 8160) in conjunction with a Leeds and Northrup "Mueller" bridge, Model 9835-B, a guarded Nanovolt detector, Type 9838, and an Azar Type H recorder. This equipment enabled a change in resistance of 0.000007273 ohm (7.86×10^{-5}°) to be recorded as 0.01 of full scale on the Azar recorder paper.

Oxygen from a cylinder was passed through a purifier of four columns; the first packed with wire-form CuO at 550°, the second with Ascarite, the third with $Mg(ClO_4)_2$, and the fourth with P_2O_5.

Procedure for Calibration of the Calorimeter. The energy equivalent of the calorimeter was determined *via* the combustion of benzoic acid, National Bureau of Standards sample No. 39-i, under the standard conditions recommended by Coops, Jessup, and van Nes.[12] The benzoic acid was pelleted and mercerized cotton served as fuse. The only difference from the usual procedure was

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(9) This fact incidentally supports our earlier statement to the same effect (H. K. Hall, Jr., M. K. Brandt, and R. M. Mason, *J. Amer. Chem. Soc.*, 80, 6420 (1958)) and disposes of the remarks of Ya. I. Gol'dfarb and L. I. Balen'kii (*Russ. Chem. Rev.*, **29**, 214 (1960)). Two qualifications must be made: (1) no substituents are present, or else conformational strains in the polymer may outweigh the strain in the ring (*i.e.*, failure to polymerize does not in substituted cases mean absence of ring strain); (2) the ring must not be so large that purely statistical (entropy) factors cause polymerization.

(10) *Cf.* F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 331 (1950); **51**, 1710 (1955).

(11) H. K. Hall, Jr., to be published.

(12) J. Coops, R. S. Jessup, and K. van Nes in "Experimental Thermochemistry," F. D. Rossini, Ed., Interscience, New York, N. Y., 1965, p 27.

Table III. Determination of Energy Equivalent of Calorimeter, E_s, by Combustion of Benzoic Acid

Expt no.	Mass of benzoic acid *in vacuo*, g	ΔR_c, ohm	Δt, °C	q_i, J	q_f, J	q_n, J	E_c, J deg^{-1}	E_s, J deg^{-1}
1	1.100724	0.175781	1.736748	2.88	94.93	15.52	2.31	16,816.7
2	1.180437	0.207506	2.051271	2.13	83.60	16.73	2.93	16,812.5
3	1.248468	0.199454	1.971697	3.60	90.96	15.06	2.98	16,794.8
4	1.169664	0.186735	1.846029	2.13	92.87	20.88	2.61	16,808.9
5	1.153119	0.184128	1.820259	2.76	95.98	17.53	2.54	16,806.9
6	0.966579	0.154428	1.526695	2.76	90.33	14.48	1.78	16,804.4
7	0.965609	0.154273	1.525159	2.34	93.26	13.89	1.78	16,805.8
							Av	16,807.1 ± 4.9

Table IV

Expt no.	Mass film *in vacuo*, g	ΔR_c, ohm	Δt, °C	q_i, J	q_f, J	q_n, J	E_s, J deg^{-1}	E_c, J deg^{-1}	$-\Delta U_B/m_a$, J, g^{-1}
1	0.616070	0.172328	1.703355	3.01	94.52	4.02	16,808.0	3.96	46,310
2	0.527113	0.148468	1.466834	3.31	90.29	3.97	16,808.0	3.43	46,660
3	0.557100	0.156014	1.542409	3.56	96.61	5.15	16,808.0	3.59	46,350
								Av	46,440 ± 110

to fire the bomb at ~23° so that the projected final temperature was 25.000000°. This method was preferred because it led to linear before and after portions of the resistance time plot and made the determination of ΔR_c easy. The gaseous contents of the bomb after combustion were sampled and analyzed mass spectrometrically; no significant amount of CO, NO, or NO_2 was ever found. The liquid contents were titrated potentiometrically with 0.1 *N* NaOH to determine the amount of nitric acid formed. No soot was ever observed in the combustions.

Calibration Calculations. The calculations followed those described by Prosen[13] but for 25°. The quantity ΔU_B (25°) for

$$Q_{\text{total}} = 26{,}433.8 \text{ J g}^{-1}(m_B + q_i + q_n + q_f)$$

$$Q_{\text{total}} = (E_s + C_p m_B)\Delta t_c$$

benzoic acid sample was specified by the National Bureau of Standards as 26.4338 ± 0.0026 absolute kJ g^{-1}. The quantity m_B is the mass of benzoic acid corrected *in vacuo*. The quantity q_i was the heat evolved from ignition of the primary platinum fuse. The quantity q_n, the heat evolved from formation of 0.1 *N* nitric acid, was calculated from the value of 57.8 kJ mol^{-1}. The quantity q_f, the heat of combustion of mercerized cotton, was taken as 17.02 kJ g^{-1}. The value of C_p for benzoic acid, 1.21 J g^{-1}, was that given by Prosen.[13] The thermochemical calorie is taken equal to 4.1840 absolute J. All calculations were done in Fortran V on a Univac 1108 computer. The E_S values refer to the calorimeter plus all contents except the substances to be burned (Table III).

Heat of Combustion of Polyethylene Film. Liquid samples for combustion were sealed in three bags of medium density (0.92 g cc^{-1}), medium slip polyethylene. We preferred this to polyester film because it was much easier to seal. It was necessary to determine the heat of combustion of this particular sample (Table IV). The value of C_p at 25° was taken as 2.33 J g^{-1} deg^{-1}.[14] The quantity m_a is the mass of film corrected *in vacuo*.

Combustion of Samples. As mentioned above, the samples, all of which were liquids, were enclosed in polyethylene film.

Calculation of Heats of Combustion. We calculated $-\Delta U_{c,1}$ in kcal mol^{-1} as follows:[13,15] $-\Delta U_{c,1}° = (E_S + c_p 24° m_s)\Delta t_c - q_i - q_f - q_n - q_a + q_w(M/m_s)(10^{-3}/4.1840)$. The term C_p, $24° m_s$ is listed as E_c. The heat capacities C_p at 24° were determined for each sample using a du Pont scanning calorimeter. The Washburn correction q_w was calculated as described by Prosen[13] but for 25°, by interpolation in the constants. The value m_s is the mass of sample corrected *in vacuo*. *M* is the molecular weight of the compound. The atomic weights were the 1961 values: C, 12.0115; H, 1.00797; N, 14.0067; O, 15.9994. The enthalpy of combustion was calculated as: $\Delta H_c° = \Delta U_c° - \Delta nRT$. The values of $\Delta H_{f,g}°$ for CO_2 and H_2O were taken from Klotz,[16] leading to $\Delta H_f°_{298}$. The several values were averaged and the standard deviation was calculated. Densities were taken from Beilstein or estimated. As the heat contributed by the film was only ~10% of the total, we did not make a separate correction for the heat capacity of the film.

Enthalpies of Vaporization. Vapor pressures were measured by use of a sickle cell, a differential pressure measuring device (glass Bourdon gage).[17,18] The sickle cell pressure indicator pointer is displaced from its null point when a pressure difference exists between the open and closed parts of the cell to bring the measuring pointer to its null position, thus equalizing the pressure in both parts of the system. The pressure in the open part is then read by a McLeod gage or mercury manometer and is taken as the pressure of the closed part of the system.

Measurements were made by attaching the 225-ml cell to a vacuum system and bringing both parts of the cell to a pressure of 10^{-5} mm. The cell was then brought to atmospheric pressure by adding dry nitrogen to both parts. The specimen was introduced into the cell and frozen by immersing in a mixture of Dry Ice–acetone. While the specimen remained frozen, both sections of the cell were evacuated to a pressure of 10^{-5} mm and the sample entrance port sealed off. The cell was then allowed to reach room temperature and was placed into a controlled bath of Dow-Corning 550 silicone oil. The temperature of the bath was then brought to a constant temperature of 30 ± 0.05° and allowed to stand for 20–25 min. The pressure of the open part of the system was adjusted to match the pressure of the closed part of the system by admitting dry air. This brought the measuring pointer of the sickle cell to its null point and the pressure of the open part of the system was read. Additional pressures were read in increments of 15-20° up to the boiling point of the specimen under investigation.

Enthalpies of vaporization were calculated from

$$\Delta H_{\text{vap}} = \left[\frac{(\log P_2 - \log P_1)}{(1/T_2 - 1/T_1)}\right]2.303R$$

Plots were linear over the range studied. The vapor pressure data

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(13) See E. J. Prosen in ref 12, p 129.

(14) F. S. Dainton, D. M. Evans, F. E. Hoare, and T. P. Melia, *Polymer*, 3, 277 (1962).

(15) A. F. Bedford, J. G. Carey, I. T. Millar, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3895 (1962).

(16) I. M. Klotz, "Chemical Thermodynamics," 2nd ed, W. A. Benjamin, New York, N. Y., 1964, p 64.

(17) F. Daniels, *J. Amer. Chem. Soc.*, 50, 1115 (1928).

(18) A. W. Laubengayer and F. B. Schermer, *ibid.*, 62, 1578 (1940).

Table V. Vapor Pressures

Compound														
Cyclopropanecarbonitrile	Temp, °C	36.5	42.0	50.4	57.0	66.8	73.6	80.0	90.0	100.0	110.0	118.1		
	Vp, mm	19.0	24.0	36.9	49.0	73.0	100.1	125.0	182.0	255.0	355.0	465.0		
Bicyclobutane-1-carbonitrile	Temp, °C	33.5	36.0	41.0	42.8	49.5	50.5	58.7	67.5	72.3	74.0	76.0		
	Vp, mm	7.0	8.0	11.0	12.0	18.0	19.0	28.5	43.0	53.5	59.0	64.0		
Cyclobutanecarbonitrile	Temp, °C	54.8	60.9	69.8	79.2	92.8	108.8	118.5	128.5					
	Vp, mm	28.0	37.5	54.0	77.5	128.0	224.0	309.5	422.0					
3-Methylenecyclobutanecarbonitrile	Temp, °C	74.8	85.5	101.3	112.3	123.6	137.6	149.8	161.8					
	Vp, mm	31.9	51.0	97.0	149	219	346	495	770					
Bicyclo[2.1.0]pentane-1-carbonitrile	Temp, °C	58.5	65.3	72.5	78.0	82.0	94.8	90.0	102.8	99.0	105.0	113.0	113.3	117.2
	Vp, mm	13.0	18.0	24.0	30.0	36.0	62.0	50.0	85.0	72.0	91.0	125.0	124.0	146.0
Cyclopentanecarbonitrile	Temp, °C	66.5	74.8	84.9	94.8	105.5	115.6	124.7	134.2	145.2				
	Vp, mm	23.5	34.5	51.0	72.0	106.0	149.0	200.0	269.0	373.5				
Bicyclo[3.1.0]hexane-1-carbonitrile	Temp, °C	93.1	102.0	104.7	111.1	117.7	120.1	124.5	129.2	134.0	139.2	143.1		
	Vp, mm	36.5	45.0	45.0	58.5	85.0	83.0	109.5	115.0	145.0	165.0	196.0		
		149.4	153.0	159.0	162.0	170.7								
		236.0	263.0	295.0	335.0	425.0								
Cyclohexanecarbonitrile	Temp, °C	60.0	71.0	85.5	96.5	106.0	115.2	125.0	134.0	141.2	154.0			
	Vp, mm	11.0	16.0	27.0	44.0	65.0	89.0	125.0	163.0	206.0	299.0			
Acetonitrile	Temp, °C	26.2	31.5	36.1	40.6	45.5	52.5	57.0	62.2	69.5				
	Vp mm,	89.0	114.0	136.0	169.0	210.0	275.0	325.0	387.0	509.0				
Propionitrile	Temp, °C	35.0	44.0	50.0	58.4	66.0	72.1	77.5	82.5	85.5	89.7			
	Vp, mm	70.0	108.0	137.0	198.0	262.0	327.0	393.0	470.0	524.0	593.0			
Isobutyronitrile	Temp, °C	30.0	39.1	48.6	57.0	62.5	66.4	72.0	79.0					
	Vp, mm	44.0	69.0	103.0	147.0	186.0	219.0	262.0	341.0					
Pivalonitrile	Temp, °C	25.8	34.0	42.0	50.0	56.8	64.6	72.0	76.0	80.0	86.8	91.6		
	Vp, mm	36.0	54.0	78.0	110.0	146.0	200.0	258.0	306.0	347.0	436.0	509.0		
Acrylonitrile	No vp data were determined for this compound													
Methyl bicyclobutane-1-carboxylate	Temp, °C	25.7	32.5	42.3	49.8	58.3	63.9	71.4	78.8	85.4	90.9	97.9	104.1	
	Vp, mm	9.5	13.5	19.5	27.5	40.5	54.0	71.0	95.0	121.0	145.0	178.0	213.0	
Methyl cyclobutanecarboxylate	Temp, °C	46.0	61.0	68.5	78.0	88.0	98.5	105.0						
	Vp, mm	28.5	58.0	81.5	118.0	175.0	243.0	305.0						
Methyl formate	Temp, °C	12.0	0.0	16.0	25.5	32.0								
	Vp, mm	100	203	405	580	760								
Methyl acetate	Temp, °C	0.0	26.6	32.0	36.5	40.2	44.5							
	Vp, mm	57.0	225.0	291.0	345.0	400.0	475.0							
Methyl pivalate	Temp, °C	25.8	33.0	44.5	50.0	55.0	66.0	74.5	81.5	83.0				
	Vp, mm	43.0	59.0	101.0	122.0	148.0	232.0	318.0	403.0	435.0				
Methyl acrylate	Temp, °C	25.8	30.5	36.5	41.0	46.5	49.5	55.5	63.5					
	Vp, mm	127	150	184	218	269	301	354	475					
Methyl benzoate	Temp, °C	67.5	80.0	91.0	104.5	112.5	123.5	132.5	143.0	160.0				
	Vp, mm	6.0	17.0	25.0	43.0	58.0	80.0	111.0	157.0	259.0				

Table VI. Bicyclobutane-1-carbonitrile[a]

Expt no.	Mass sample	Δt, °C	q_i, J	q_f, J	q_n, J	q_n, J	q_w, J	E_c, J deg^{-1}	$\Delta U°$, kcal mol^{-1}
1	0.454720	1.325276	3.01	73.5	44.8	5260	8.12	0.75	−702.15
2	0.600572	1.705529	3.05	75.8	62.8	6200	11.0	0.98	−702.55
3	0.644075	1.722808	3.01	77.8	47.7	4880	12.1	1.06	−702.63
4	0.533057	1.517071	2.76	73.4	46.8	5550	9.74	0.89	−702.72
5	0.758336	2.012887	3.68	71.2	54.7	5540	14.6	1.25	−701.93
6	0.670831	1.797764	3.56	69.9	52.4	5150	12.7	1.12	−702.75

Temp, °C	33.5	36.0	41.0	42.8	49.5	50.5	58.7	67.5	72.3	74.0	76.0
Vp, mm	7.0	8.0	11.0	12.0	18.0	19.0	28.5	43.0	53.5	59.0	64.0

Results, kcal mol^{-1}					
$\Delta U_c°$	Δn	$\Delta H_{c,1}°$	$\Delta H_{f,1}°$	$\Delta H_{vap}°$	$\Delta H_{f,g}°$
−702.46 ±0.28	−0.75	−702.90	+61.85	+10.93	+72.78

[a] C_5H_5N; mol wt 79.102; E_s 16808.0 J deg^{-1}; C_p 1.67 J deg^{-1} g^{-1}; $d^{20}{}_4$ 0.9 g ml^{-1} est.

are collected in Table V. A representative collection of experimental data is given for bicyclobutane-1-carbonitrile in Table VI.

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