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Calorimetric and Computational Study of 3-Buten-1-ol and 3-Butyn-1-ol. Estimation of the Enthalpies of Formation of 1-Alkenols and 1-Alkynols

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The enthalpies of combustion and vaporization of 3-buten-1-ol and 3-butyn-1-ol have been measured by static bomb combustion calorimetry and correlation gas chromatography techniques, respectively, and the gas-phase enthalpies of formation, $\Delta_f H^\circ_m(g)$, have been determined, the values being −147.3 ± 1.8 and 16.7 ± 1.6 kJ mol^{-1}, for 3-buten-1-ol and 3-butyn-1-ol, respectively. High level calculations at the G2 and G3 levels have also been carried out. Relationships between the enthalpies of formation of 1-alkanols, 1-alkenols and 1-alkynols and with the corresponding hydrocarbons have been discussed. From the calculated contributions to $\Delta_f H^\circ_m(g)$ for the substitutions of CH_3 by CH_2OH, CH_3CH_2 by $CH_2{=}CH$ and CH_3CH_2 by $CH{\equiv}C$, we have estimated the $\Delta_f H^\circ_m(g)$ values for 3-buten-1-ol and 3-butyn-1-ol, in excellent agreement with the experimental ones. $\Delta_f H^\circ_m(g)$ values for 1-alkenols and 1-alkynols up to 10 carbon atoms have also been estimated.

Introduction

The structure and energetics of molecules are fundamental concepts in chemistry, the energy associated with a particular structure being related to the constituent atoms, and the corresponding bond and angles that form the molecular framework.[1] Thermodynamic data such as the enthalpies of formation are often helpful in the understanding of the structural, conformational, and reactivity trends exhibited by the molecules. One of the purposes of thermochemistry is to derive the enthalpies of formation of compounds from their elements and to relate them to structure and chemical binding.[1−3]

The enthalpies of formation in the gas phase, $\Delta_f H^0_m(g)$, have been measured for a large number of alkanols;[4−6] however, the values measured for alkenols and alkynols are very scarce. In Pedley's compilation,[5] there is only one alkenol, 2-propen-1-ol ($\Delta_f H^0_m(g) = -124.5 \pm 1.8$ kJ mol^{-1}), and there is not one alkynol. In the NIST database,[6] there are also values for ethenol and ethynol.

In this work we have carried out the experimental determination of the enthalpies of formation in the gas phase of 3-buten-1-ol and 3-butyn-1-ol. We have also carried out a theoretical study calculating the $\Delta_f H^0_m(g)$ values for both alcohols and also for 1-butanol at two high computational levels, G2 and G3. Relationships between the enthalpies of formation of alkanes, 1-alkenes, 1-alkynes, 1-alkanols, 1-alkenols, and 1-alkynols are discussed with the purpose to derive different contributions that permit the estimation of unknown $\Delta_f H^0_m(g)$ values for 1-alkenols and 1-alkynols from known values of the other type of compounds.

Experimental Section

Material and Purity Control. 3-Buten-1-ol and 3-butyn-1-ol were commercially available from Lancaster (mass fraction 0.99 and 0.97, respectively). Both compounds were dried over molecular sieves. 3-Buten-1-ol was distilled three times, bp = 60 °C/135 mmHg, and 3-butyn-1-ol twice, bp = 88 °C/184 mmHg. Determination of purities, assessed by gas chromatography and mass spectrometry indicated that the mole fractions of 3-buten-1-ol and 3-butyn-1-ol were better than 0.999 and 0.988, respectively. The content of water was assessed by mass spectrometry and Karl-Fisher analysis giving the values 0.2419% and 0.2796% for 3-buten-1-ol and 3-butyn-1-ol respectively

Procedure for Thermochemical Measurements. An isoperibol calorimeter equipped with a static combustion bomb was used for the measurements of the energy of combustion. The apparatus and procedure have been described in ref 7. The initial temperature of the combustion experiments was chosen so that the final calorimeter temperature would be near 298.15 K, and the energy of reaction was always referenced to the final temperature of 298.15 K. The energy equivalent of the calorimeter, ϵ(calor), was determined from the combustion of benzoic acid, NIST standard reference sample 39j, having a massic energy of combustion, $\Delta_c u$, under the conditions specified on the certificate, of −26434 ± 3 J g^{-1}. From six calibration experiments $\epsilon(\text{calor}) = 14283.14 \pm 0.98$ J K^{-1}, where the uncertainty quoted is the standard deviation of the mean. Frequent calibration experiments were made throughout the series of combustion experiments.

The energy of combustion of 3-buten-1-ol and 3-butyn-1-ol was determined by burning the liquid samples in polyethylene ampules in a platinum crucible. In all the experiments 1 cm^3 of water was added to the bomb. The combustion bomb was flushed and filled with oxygen to a pressure of $p = 3.04$ MPa. Under these conditions no carbon or CO were found. The empirical formula and massic energy of combustion of our cotton-thread fuse and polyethylene were $C_{1.000}H_{1.740}O_{0.871}$ and −17410 ± 37 J g^{-1} and $C_{0.968}H_{2.000}$ and −46339.3 ± 6.6 J g^{-1}, respectively, and were determined in the Madrid laboratory. The nitric acid content in the bomb liquid was determined by titration

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TABLE 1: Physical Properties at $T = 298.15$ K (Values in Parentheses Were Estimated)

compound	M, g mol^{-1}	ρ, g cm^{-3}	$(\delta V/\delta T)_p \times 10^{-7}$, dm^3 g^{-1} K^{-1}	c_p, J K^{-1} g^{-1}
cotton	27.700	1.5	9.69[a]	1.48
polyethylene	13.6422	0.9187[b]	0.248[b]	2.0[b]
3-buten-1-ol	72.1057	0.8424[c]	(3.354)	2.513[d]
3-butyn-1-ol	70.0898	0.9257[c]	(3.354)	2.611[d]

[a] Value taken from ref 9. [b] Properties are those given by the supplier. [c] Value taken from ref 10. [d] Measured by DSC in our laboratory, in Madrid.

with 0.1 mol dm^{-3} NaOH(aq). The corrections for nitric acid formation[8] were based on -59.7 kJ mol^{-1} for the standard molar energy of formation of 0.1 mol dm^{-3} HNO_3(aq) from N_2(g), O_2(g), and H_2O(l). All samples were weighed with a Mettler AT-21 microbalance, and corrections of apparent mass to mass were made. After disassembly of the calorimeter, the bomb gases were slowly released and the absence of CO was checked with Dragër tubes (sensitivity levels were approximately 1×10^{-6} mass fraction). For the correction of apparent mass to mass, conversion of the energy of the actual bomb process to that of the isothermal process, and correction to standard states, we have used the values of density ρ, massic heat capacity c_p, and $(dV/dT)_p$, respectively, given in Table 1.

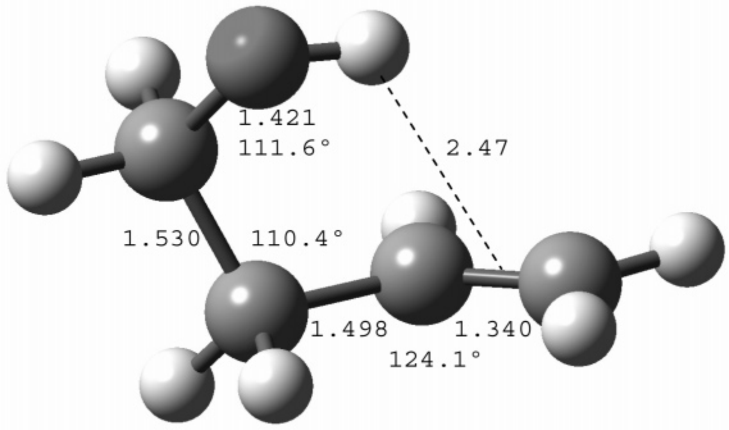
Corrections to standard states were made according to Hubbard et al.[11] The atomic weights of the elements were those recommended by IUPAC in 1999.[12]

The enthalpies of vaporization of 3-buten-1-ol and 3-butyn-1-ol were determined by correlation gas chromatography experiments following the method developed and described by Chickos et al. in ref 13. The experiments were carried out with a Hewlett-Packard gas chromatograph, model 5890 Series II, equipped with a split/splitless capillary injection port and a flame ionization detector (FID). An HP-5 (60 m × 0.25 mm × 0.25 μm) fused silica capillary column was used. Nitrogen was used as carrier gas with column head pressure of 93.1 kPa. Methane was used as unretained compound to calculate the net retention time. Analyses were performed using a split injection ratio of $\approx$ 150:1. The detector and injector were maintained at 523.15 K in all the experiments. *n*-Propanol, *n*-butanol, *n*-pentanol, *n*-hexanol, and *n*-heptanol were used as reference standards. For all these compounds, the enthalpies of vaporization at 298.15 K are well-known and are given in ref 14.

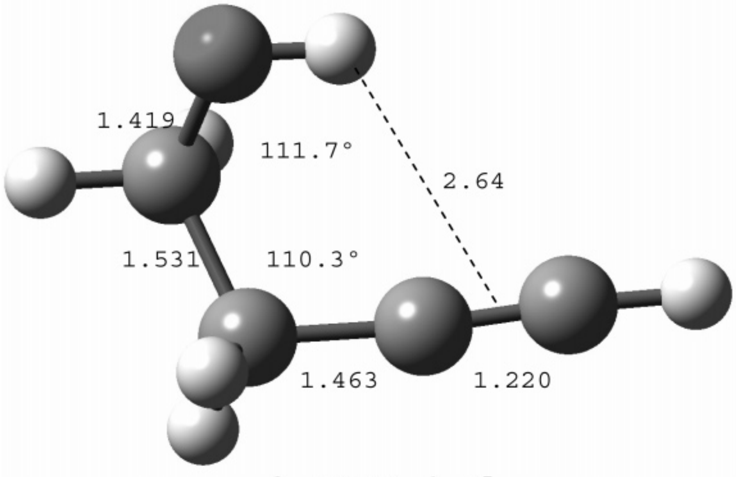
Isothermal gas chromatograms were obtained over a 50 K range every 5 K. To check the quality of our measurements the enthalpies of vaporization of 2-propanol, 3-methyl-1-butanol, 3-pentanol, and 2-methyl-2-pentanol were also determined and the results are compared with the values given in the literature.[14]

Computational Details. Standard ab initio molecular orbital calculations[15] were performed with the Gaussian03 series of programs.[16] The energies of the studied compounds were calculated using Gaussian-n theories, at the G2[17] and G3[18] levels.

G2 corresponds effectively to calculations at the QCISD(T)/6-311+G(3df,2p) level on MP2(full)/6-31G(d) optimized ge-



3-Buten-1-ol



3-Butyn-1-ol

Figure 1. MP2(FULL)/6-31G(d)-optimized structures of 3-buten-1-ol and 3-butyn-1-ol. Bond lengths are given in ångstroms and bond angles in degrees.

TABLE 2: Results of Combustion Experiments of 3-Buten-1-ol and 3-Butyn-1-ol at $T = 298.15$ K[a]

	3-Buten-1-ol				
m'(compound), g[b]	0.416534	0.408178	0.398227	0.361814	0.383624
m''(polyethylene), g[b]	0.331699	0.253363	0.229437	0.228595	0.239913
m''' (fuse), g[b]	0.002682	0.002664	0.002434	0.002262	0.002205
ΔT_c, K = $(T_f - T_i + \Delta T_{corr})$, K	2.0945	1.8210	1.7186	1.6271	1.7173
ϵ(calor)$(-\Delta T_c)$, kJ[c]	−29.9155	−26.0102	−24.5475	−23.2400	−24.5281
ϵ(cont)$(-\Delta T_c)$, kJ[d]	−0.0360	−0.0305	−0.0285	−0.0267	−0.0285
ΔU_{ign}, kJ[e]	0.0008	0.0008	0.0008	0.0008	0.0008
ΔU_{dec} (HNO_3), kJ[f]	0.0022	0.0020	0.0015	0.0014	0.0014
ΔU(corr to std states), kJ[g]	0.0099	0.0086	0.0080	0.0075	0.0080
$-m''\Delta_c u°$(polyethylene), kJ	15.3707	11.7406	10.6319	10.5929	11.1174
$-m'''\Delta_c u°$(fuse), kJ	0.0468	0.0464	0.0424	0.0394	0.0384
$\Delta_c u°$(compound), kJ g^{-1}	−34.8617	−34.8924	−34.8831	−34.8928	−34.9055
$\langle \Delta_c u°(298.15\ \mathrm{K}) \rangle$, kJ g^{-1}	−34.8871 ± 0.0073				
	3-Butyn-1-ol				
m'(compound), g[b]	0.429284	0.446013	0.465673	0.385015	0.474149
m''(polyethylene), g[b]	0.297539	0.334595	0.295617	0.306274	0.288283
m'''(fuse), g[b]	0.002768	0.002681	0.002599	0.002425	0.002768
ΔT_c, K = $(T_f - T_i + \Delta T_{corr})$, K	1.9941	2.1534	2.0747	1.9159	2.0709
ϵ(calor)$(-\Delta T_c)$, kJ[c]	−28.4827	−30.7574	−29.6330	−27.3657	−29.5784
ϵ(cont)$(-\Delta T_c)$, kJ[d]	−0.0341	−0.0372	−0.0358	−0.0325	−0.0357
ΔU_{ign}, kJ[e]	0.0008	0.0008	0.0008	0.0008	0.0008
ΔU_{dec}(HNO_3), kJ[f]	0.0014	0.0023	0.0017	0.0021	0.0021
ΔU(corr to std states), kJ[g]	0.0108	0.0117	0.0114	0.0101	0.0114
$-m''\Delta_c u°$(polyethylene), kJ	13.7877	15.5049	13.6987	14.1925	13.3588
$-m'''\Delta_c u°$(fuse), kJ	0.0483	0.0467	0.0453	0.0423	0.0483
$\Delta_c u°$(compound), kJ g^{-1}	−34.1681	−34.1430	−34.1675	−34.1556	−34.1511
$\langle \Delta_c u°(298.15\ \mathrm{K}) \rangle$, kJ g^{-1}	−34.1571 ± 0.0048				

[a] For a definition of the symbols see refs 11 and 29. $T_{th} = 298.15$ K; $V_{bomb} = 0.380$ dm^3; $p^i_{gas} = 3.04$ MPa; $m^i_{water} = 1.00$ g. [b] Masses obtained from apparent mass. [c] ϵ(calor), energy equivalent of the whole system but the content of the bomb. [d] ϵ(cont), energy equivalent of the contents of the bomb $\epsilon(\mathrm{cont})(-\Delta T_c) = \epsilon^i(\mathrm{cont})(T^i - 298.15\ \mathrm{K}) + \epsilon^f(\mathrm{cont})(298.15\ \mathrm{K} - T^f + \Delta T_{corr})$. [e] Experimental energy of ignition. [f] Experimental energy of formation of nitric acid. [g] ΔU(corr to std states) is the sum of items 81−85, 87−90, 93, and 94 in ref 11.

ometries, incorporating scaled HF/6-31G(d) zero-point vibrational energies and a so-called higher-level correction to accommodate remaining deficiencies.

The scheme of G3 theory is similar to that of G2, but the MP2 single-point energy calculation is performed with a new basis set, referred to as G3large that includes core correlation. So, G3 is effectively at the QCISD(T,full)/G3large level, making certain assumptions about the additivity of the calculations. It also includes a spin−orbit correction for atomic species only. The higher-level empirical correction is now different for atoms and for molecules.

TABLE 3: Standard Molar Energy of Combustion and Enthalpies of Combustion and Formation at $T = 298.15$ K

compound	$\Delta_c U°_m$, kJ mol^{-1}	$\Delta_c H°_m$, kJ mol^{-1}	$\Delta_f H°_m$(l), kJ mol^{-1}
3-buten-1-ol	−2515.56 ± 1.44	−2519.29 ± 1.44	−198.07 ± 1.54
3-butyn-1-ol	−2394.06 ± 1.15	−2396.56 ± 1.15	−34.97 ± 1.27

Results

Molecular Structures. The conformational composition of 3-buten-1-ol and 3-butyn-1-ol have been the subject of a number of investigations. The question of intramolecular OH···π hydrogen bonding has been central to these studies. Schleyer et al.[19] was the first to report evidence which demonstrated the occurrence of intramolecular hydrogen bonding between proton donors and unsaturated linkages, including double and triple bonds. This conclusion was based in the presence of two bands in the OH region in the IR spectrum of certain alkenols and alkynols. Trætteberg and Østensen,[20] in an electron diffraction investigation of the structure of 3-buten-1-ol found that the major conformer in the gas-phase had a geometry that made intramolecular hydrogen bonding possible; Marstokk and Møllendal[21] agreed with this result in a microwave spectroscopy investigation. More recently, Bakke and Bjerkeseth[22] have studied the conformational composition of 3-buten-1-ol by a combination of IR and ^{1}H NMR spectroscopy; Crofts et al.,[23] by free expansion jet spectroscopy; and Kowski et al.[24] by UV photoelectron spectroscopy. Theoretical calculations at different levels have also been carried out.[22,23,25] All of these experimental and theoretical studies have confirmed that the most stable conformer of 3-buten-1-ol is a gauche one stabilized by an intramolecular hydrogen bond from the OH hydrogen to the π cloud. The structure obtained in this work, optimized at the MP2(FULL)/6-31G(d) level, is shown in Figure 1, and it is in accordance with that previously determined.

Studies on the molecular structure of 3-butyn-1-ol have been carried out by Szalanski and Ford,[26] by microwave spectroscopy; by Bakken et al.,[27] by gas electron diffraction; by Kowski et al.[24] by UV photoelectron spectroscopy; and, very recently, by Slagle et al.,[28] by microwave spectroscopy. In the last two reports, theoretical calculations have also been carried out. All of these experimental and theoretical studies have confirmed the intramolecular π-hydrogen bond between the hydroxyl hydrogen atom and the triple bond. The most stable conformer of 3-butyn-1-ol presents a gauche conformation in order to allow the energetically favorable hydrogen bond. The structure obtained in this work, optimized at the MP2(FULL)/6-31G(d) level, is also shown in Figure 1, and it is in accordance with that previously determined.

Experimental Determination of the Enthalpies of Formation. The results of combustion experiments for 3-buten-1-ol and 3-butyn-1-ol are given in Table 2.

The experimental values have been derived as in ref 11. The energy of solution of carbon dioxide in water at 298.15 K, $\Delta_{sol}U(CO_2)$, was taken as −17.09 kJ mol^{-1}, and the solubility constant, $K(CO_2)$, as 0.03440 mol dm^{-3} atm^{-1} at 298.15 K.[8]

Table 3 gives the molar energies and enthalpies of combustion derived from the combustion reactions of 3-buten-1-ol and

TABLE 4: GC Retention Times of Alcohols (min) vs Temperature (K)

	retention times of alcohols (min)										
compound	$T =$ 343.15 K	$T =$ 348.15 K	$T =$ 353.15 K	$T =$ 358.15 K	$T =$ 363.15 K	$T =$ 368.15 K	$T =$ 373.15 K	$T =$ 378.15 K	$T =$ 383.15 K	$T =$ 388.15 K	$T =$ 393.15 K
methane	5.930	5.990	6.060	6.130	6.190	6.260	6.314	6.380	6.440	6.502	6.553
1-propanol	6.710	6.680	6.670	6.675	6.690	6.710	6.730	6.750	6.780	6.815	6.840
1-butanol	7.750	7.575	7.440	7.340	7.260	7.210	7.170	7.140	7.130	7.115	7.110
1-pentanol	10.070	9.510	9.065	8.715	8.430	8.217	8.040	7.890	7.780	7.690	7.610
1-hexanol	15.110	13.630	12.460	11.525	10.770	10.187	9.700	9.300	8.980	8.725	8.505
1-heptanol	26.065	22.395	19.530	17.265	15.460	14.047	12.910	11.980	11.230	10.620	10.120
2-propanol	6.390	6.403	6.437	6.470	6.500	6.542	6.578	6.620	6.663	6.707	6.740
3-methyl-1-butanol	9.140	8.740	8.433	8.183	7.980	7.833	7.713	7.610	7.537	7.493	7.430
3-pentanol	8.390	8.120	7.907	7.750	7.610	7.510	7.427	7.373	7.330	7.300	7.273
2-methyl-2-pentanol	9.110	8.723	8.420	8.187	7.980	7.830	7.703	7.613	7.537	7.487	7.433
3-buten-1-ol	7.430	7.310	7.220	7.157	7.100	7.073	7.040	7.037	7.040	7.040	7.043
3-butyn-1-ol	7.560	7.407	7.300	7.230	7.157	7.120	7.083	7.073	7.067	7.070	7.063

TABLE 5: Parameters of the Straight Lines ln(1/t_r) vs 1/T

alcohol	A^a	B^b	r^2
1-propanol	8.04851	−2670.11942	0.99907
1-butanol	8.68490	−3180.54958	0.99963
1-pentanol	9.28269	−3666.34807	0.99967
1-hexanol	9.95536	−4170.14153	0.99971
1-heptanol	10.61522	−4665.63259	0.99973
2-propanol	7.74768	−2389.29544	0.99942
3-methyl-1-butanol	8.98360	−3476.55511	0.99955
3-pentanol	8.76368	−3311.08462	0.99971
2-methyl-2-pentanol	8.93531	−3457.86554	0.99972
3-buten-1-ol	8.39474	−3015.84886	0.99963
3-butyn-1-ol	8.59256	−3110.40132	0.99957

[a] Intercept. [b] Slope.

3-butyn-1-ol, in the crystalline state at $T = 298.15$ K, which correspond to reaction 1 for the former and to reaction 2 for the latter.

$$C_4H_8O(l) + {}^{11}/{}_{2}O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l) \qquad (1)$$

$$C_4H_6O(l) + 5O_2(g) \rightarrow 4CO_2(g) + 3H_2O(l) \qquad (2)$$

In accordance with the normal thermochemical practice, the uncertainties assigned are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration.[30] To derive $\Delta_f H°_m(l)$ from $\Delta_c H°_m(l)$, the standard molar enthalpies of formation of $H_2O(l)$ and $CO_2(g)$, at $T =$ 298.15 K, −285.830 ± 0.042 and −393.51 ± 0.13 kJ mol^{-1}, respectively, were used.[31]

Table 4 gives the GC retention times of alcohols vs temperature in the interval from 343.15 to 393.15 K. The net retention times t_r for each compound were calculated by subtracting the retention time of the unretained compound, methane.

Table 5 gives the parameters of the straight lines obtained when ln(1/t_r) is plotted vs 1/(T/K), and in all the cases, the correlation coefficient was >0.99, indicating no retention was happening.

The values corresponding to $\Delta_{sol}{}^{g}H_m$ were obtained when the slope of these lines are multiplied by the gas constant R, and they are given in Table 6. A plot of the vaporization enthalpies of the standards $\Delta_l{}^{g}H_m$(298.15 K) against the corresponding values of $\Delta_{sol}{}^{g}H_m(T_m)$, with T_m being the mean temperature of the experiments, resulted in the linear relationship given at the bottom of Table 6. Values of $\Delta_l{}^{g}H_m$calculated from this equation for the reference substances 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol and for the test compounds 2-propanol, 3-methyl-1-butanol, 3-pentanol, and 2-methyl-2-pentanol are given in the fourth column of Table 6. The fifth column gives their difference with the published values expressed as percentages.

The values of $\Delta_l{}^{g}H_m$(298.15 K) for both 3-buten-1-ol and 3-butyn-1-ol were obtained from the correlation equation and their respective $\Delta_{sol}{}^{g}H_m$, and they are 50.79 ± 0.88 kJ mol^{-1} and 51.70 ± 0.88 kJ mol^{-1} respectively.

The standard molar enthalpies of vaporization and formation in liquid and gaseous states for 3-buten-1-ol and 3-butyn-1-ol at $T = 298$ K are summarized in Table 7.

Theoretical Enthalpies of Formation. To our knowledge, there is only one previous calculation of the enthalpy of formation of 3-buten-1-ol, reported in a theoretical study on combustible gases.[32] The value obtained was −147.3 kJ mol^{-1},

TABLE 6: Enthalpies of Vaporization of Alcohols

alcohol	$\Delta_{sol}{}^{g}H_m$, kJ mol^{-1}	$\Delta_l{}^{g}H_m$(298.15K),^{a,b} kJ mol^{-1}	$\Delta_l{}^{g}H_m$(calc)^c, kJ mol^{-1}	diff, %
1-propanol	22.20	47.50 ± 0.16	47.47 ± 0.88	−0.06
1-butanol	26.44	52.42 ± 0.26	52.37 ± 0.88	−0.10
1-pentanol	30.48	57.04 ± 0.20	57.04 ± 0.88	0.00
1-hexanol	34.67	61.61 ± 0.20	61.87 ± 0.88	0.42
1-heptanol	38.79	66.81 ± 0.20	66.63 ± 0.88	−0.27
2-propanol	19.87	45.48 ± 0.24	44.78 ± 0.88	−1.54
3-methyl-1-butanol	28.91	55.63 ± 0.12	55.21 ± 0.88	−0.75
3-pentanol	27.53	54.03^d	53.63 ± 0.88	−0.74
2-methyl-2-pentanol	28.75	54.82 ± 0.04	55.03 ± 0.88	0.38
3-buten-1-ol	25.08		50.79 ± 0.88	
3-butyn-1-ol	25.86		51.70 ± 0.88	

$$\Delta_l{}^{g}H_m(298.15\ K) = (21.84 \pm 0.44) + (1.15 \pm 0.01)\ \Delta_{sol}{}^{g}H_m;\ r^2 = 0.9998$$

[a] Values taken from ref 14. [b] Uncertainties taken as two standard deviations of $\Delta_l{}^{g}H_m$(298.15 K) correlations from ref 14. [c] The uncertainty of these values was calculated as twice the uncertainty in the intercept of the correlation equation. [d] Uncertainty not available.

SCHEME 1: Experimental $\Delta\Delta_f H^0_m$(g) Values, in kJ mol^{-1}, for the Transformations between 1-Butanol, 3-Buten-1-ol, 3-Butyn-1-ol, and the Corresponding Hydrocarbons

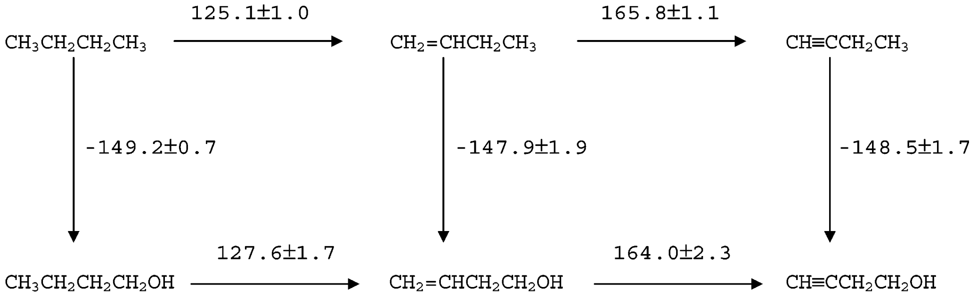


TABLE 7: Standard Molar Enthalpies at T = 298.15 K

compound	$\Delta_f H°_m$(cr), kJ mol^{-1}	$\Delta_l^g H_m$, kJ mol^{-1}	$\Delta_f H°_m$(g), kJ mol^{-1}
3-buten-1-ol	−198.07 ± 1.54	50.79 ± 0.88	−147.28 ± 1.77
3-butyn-1-ol	−34.97 ± 1.27	51.70 ± 0.88	16.73 ± 1.55

TABLE 8: G2 and G3 Total Energies at 0 K, and Enthalpies at 298 K, of the Studied Molecules, with All Values in hartrees (1 hartree = 2625.5 kJ mol^{-1})

	G2		G3	
species	E_0	H_{298}	E_0	H_{298}
1-butanol	−233.21459	−233.20663	−233.44605	−233.43810
3-buten-1-ol	−232.00542	−231.99826	−232.23581	−232.22865
3-butyn-1-ol	−230.77841	−230.77161	−231.00804	−231.00124

at the G2(MP2) level, and it was corrected to −142.3 kJ mol^{-1}, using an atom additive type correction.

In this work, we have carried out a theoretical study at the G2 and G3 levels. Calculated energies at 0 K and enthalpies at 298 K for 3-buten-1-ol and 3-butyn-1-ol are given in Table 8. Values for 1-butanol were also calculated for comparison purposes, and they are given in the same table.

In standard Gaussian-n theories, theoretical enthalpies of formation are calculated through atomization reactions, eqs 3−5, for 1-butanol, 3-buten-1-ol, and 3-butyn-1-ol, respectively. We have detailed this method in previous studies.[33,34]

$$C_4H_{10}O(g) \rightarrow 4C(g) + 10H(g) + O(g) \tag{3}$$

$$C_4H_8O(g) \rightarrow 4C(g) + 8H(g) + O(g) \tag{4}$$

$$C_4H_6O(g) \rightarrow 4C(g) + 6H(g) + O(g) \tag{5}$$

Raghavachari et al.[35] have proposed to use a standard set of isodesmic reactions, the "bond separation reactions",[15] to derive the theoretical enthalpies of formation. This method has been detailed in previous studies.[33,34]

The bond separation reactions are

$$C_4H_{10}O(g) + 3CH_4(g) \rightarrow 3C_2H_6(g) + CH_3OH(g) \tag{6}$$

for 1-butanol,

$$C_4H_8O(g) + 3CH_4(g) \rightarrow 2C_2H_6(g) + C_2H_4(g) + CH_3OH(g) \tag{7}$$

for 3-buten-1-ol, and

$$C_4H_6O(g) + 3CH_4(g) \rightarrow 2C_2H_6(g) + C_2H_2(g) + CH_3OH(g) \tag{8}$$

for 3-butyn-1-ol.

TABLE 9: Calculated Enthalpies of Formation for the Studied Compounds at the G2 and G3 Levels Using Both Atomization and Bond Separation Isodesmic Reactions, with All Values in kJ mol^{-1}

	G2		G3		
compound	atomiz	bond sep	atomiz	bond sep	exptl
1-butanol	−279.1	−277.0	−276.3	−276.6	−274.9 ± 0.4[a]
3-buten-1-ol	−155.7	−156.8	−155.2	−156.2	−147.3 ± 1.8[b]
3-butyn-1-ol	15.8	10.5	13.0	9.7	16.7 ± 1.6[b]

[a] Taken from ref 5. [b] This work.

TABLE 10: Energy Differences between the Two Most Stable Structures Relative to That with a Intramolecular Hydrogen Bond

	ΔE, kJ mol^{-1}	
compound	MP2/6-31G(d)	MP2/6-31+G(d)
3-buten-1-ol	9.2	6.9
3-butyn-1-ol	7.5	5.9
4-penten-1-ol	6.2	2.9
4-pentyn-1-ol	6.6	3.7
5-hexen-1-ol	1.6	−2.5
5-hexyn-1-ol	0.7	−2.7

TABLE 11: Estimated $\Delta_f H^0_m$(g) Values for 3-Buten-1-ol and 3-Butyn-1-ol Using the Contributions to $\Delta_f H°_m$(g) Calculated for the Substitutions of CH_3 by CH_2Oh, CH_3CH_2 by $CH_2 = CH$, and CH_3CH_2 by CH≡C (Equations 9−11)

	$\Delta_f H^0_m$(g)		
from	estimated	mean value	exptl[a]
	CH_2═$CHCH_2CH_2OH$		
$CH_3(CH_2)_2CH_3$	−148.3		
CH_2═$CHCH_2CH_3$	−148.8	−148.8 ± 0.5	−147.3 ± 1.8
$CH_3(CH_2)_2CH_2OH$	−149.2		
	CH≡CCH_2CH_2OH		
$CH_3(CH_2)_2CH_3$	16.5	16.4 ± 0.7	16.7 ± 1.6
CH≡CCH_2CH_3	17.0		
$CH_3(CH_2)_2CH_2OH$	15.6		

[a] This work.

The calculated values for the enthalpies of formation of the three compounds, at the G2 and G3 levels, using both atomization and isodesmic bond separation reactions,[36] are shown in Table 9. There is a reasonable agreement between experimental and calculated values, within the uncertainties associated with Gaussian-n methods.

Discussion

The experimental gas-phase enthalpies of formation of 3-buten-1-ol and 3-butyn-1-ol measured in this work allow us to establish a relationship between the different linear 4 carbon hydrocarbons and alcohols, as depicted in Scheme 1.

The $\Delta\Delta_f H^0_m$(g) values presented in Scheme 1 seem to indicate that the stabilization introduced in a hydrocarbon molecule when a terminal CH_3 group is substituted by CH_2OH is independent

TABLE 12: Estimated $\Delta_f H^\circ_m$(g) Values for 1-Alkenols and 1-Alkynols Using Equations 9−11

1-alkenol	$\Delta_f H^\circ_m$(g), kJ mol^{-1} calcd	$\Delta_f H^\circ_m$(g), kJ mol^{-1} expt	1-alkynol	$\Delta_f H^\circ_m$(g), kJ mol^{-1} calcd	$\Delta_f H^\circ_m$(g), kJ mol^{-1} expt
2-propen-1-ol	−128.3 ± 1.1	−124.5 ± 1.8[a]	2-propyn-1-ol	36.4 ± 1.1	
3-buten-1-ol	−148.8 ± 0.5	−147.3 ± 1.8[b]	3-butyn-1-ol	16.4 ± 0.7	16.7 ± 1.6[b]
4-penten-1-ol	−169.6 ± 0.3		4-pentyn-1-ol	−4.7 ± 0.6	
5-hexen-1-ol	−189.9 ± 0.4		5-hexyn-1-ol	−25.4 ± 0.7	
6-hepten-1-ol	−210.5 ± 0.3		6-heptyn-1-ol	−45.4 ± 0.8	
7-octen-1-ol	−230.2 ± 0.8		7-octyn-1-ol	−66.4 ± 1.2	
8-nonen-1-ol	−250.8 ± 0.1		8-nonyn-1-ol	−86.1 ± 0.1	
9-decen-1-ol	−271.5 ± 0.6		9-decyn-1-ol	−106.7 ± 0.6	

[a] Taken from ref 5. [b] This work.

of whether the hydrocarbon is an *n*-alkane, an 1-alkene or an 1-alkyne. This conclusion implies that the weak intramolecular hydrogen bond from the OH hydrogen to the π-bond charge cloud that exists in 3-buten-1-ol and 3-butyn-1-ol does not significantly influence the enthalpy of formation of these species. In 1-butanol, an intramolecular hydrogen bond to a π cloud is not possible and yet the stabilization is similar. Also, the enthalpy of hydrogenation of 3-buten-1-ol, −127.6 ± 1.7 kJ mol^{-1}, equals that of 1-butene, −125.1 ± 1.0 kJ mol^{-1}, and that of 3-butyn-1-ol, −291.6 ± 1.6 kJ mol^{-1}, equals that of 1-butyne, −290.9 ± 1.0 kJ mol^{-1}. It follows that in these compounds the OH group is sufficiently distant from the unsaturated group that it has no influence upon it. So, the thermochemical evidences suggest that 1-alkenols and 1-alkynols are not significantly stabilized with respect to their 1-alkanol homologues, the magnitude of the interaction associated with the formation of intramolecular hydrogen bonds being, at best, small.

With the purpose to rationalize this behavior we have optimized the most stable structures, with and without intermolecular hydrogen bond, for the 1-alkenols and 1-alkynols from four to six C atoms. The energy differences between both structures for each one of the compounds are shown in Table 10.

There are experimental evidences that in the case of 3-buten-1-ol,[20−24] 3-butyn-1-ol, [24,26−28] 4-penten-1-ol,[37] and 4-pentyn-1-ol,[38] the most stable conformer is a gauche one stabilized by an intramolecular hydrogen bond from the OH hydrogen to the π cloud. To our knowledge, there is not any experimental study on 5-hexen-1-ol and 5-hexyn-1-ol.

As it can be seen in Table 10, at the MP2/6-31G(d) level of theory all the structures with hydrogen bond are more stables that those without it, but the differences decrease when the number of carbon atoms increases. When the calculations are carried out at the MP2/6-31+G(d) level, that includes diffuse functions, important for the characterization of hydrogen bonds, and the differences decrease, and even in the cases of 5-hexen-1-ol and 5-hexyn-1-ol, the structures without intramolecular hydrogen bond are slightly more stable. These results suggest that the stabilization introduced by the hydrogen bond is small and decreases when the length of the chain increases.

An interesting way in which experimental data may be examined is via calculations of energies for converting one group, such as methyl, to another. Group interconversion is more satisfactory than replacement of a hydrogen by a functional group since nonbonded interactions will cancel to some extent in the former case but not in the latter.[39]

Following the ideas of Stull et al.,[40] Wiberg et al.,[41] and Slayden and Liebman,[4] we have calculated the variation in the enthalpy of formation when an *n*-alkane is converted into an 1-alkene, an 1-alkyne, or an 1-alkanol, maintening the same number of C atoms in the molecule, using all the available data collected in ref 11. The values obtained are

$$\Delta\Delta_f H^\circ_m[\mathrm{CH_3 \rightarrow CH_2OH,(g)}] = \Delta_f H^\circ_m[\mathrm{R{-}CH_2OH,(g)}] - \Delta_f H^\circ_m[\mathrm{R{-}CH_3,(g)}] = -148.32 \pm 1.2\ \mathrm{kJ\ mol^{-1}} \quad (n = 12)^{42} \quad (9)$$

$$\Delta\Delta_f H^\circ_m[\mathrm{CH_3CH_2 \rightarrow CH_2{=}CH,(g)}] = \Delta_f H^\circ_m[\mathrm{R{-}CH{=}CH_2,(g)}] - \Delta_f H^\circ_m\ [\mathrm{R{-}CH_2CH_3,(g)}] = 125.68 \pm 0.8\ \mathrm{kJ\ mol^{-1}} \quad (n = 9) \quad (10)$$

$$\Delta\Delta_f H^\circ_m[\mathrm{CH_3CH_2 \rightarrow CH{\equiv}C,(g)}] = \Delta_f H^\circ_m[\mathrm{R{-}C{\equiv}CH,(g)}] - \Delta_f H^\circ_m[\mathrm{R{-}CH_2CH_3,(g)}] = 290.43 \pm 1.0\ \mathrm{kJ\ mol^{-1}} \quad (n = 8) \quad (11)$$

The calculated $\Delta\Delta_f H^\circ_m[\mathrm{CH_3 \rightarrow CH_2OH,(g)}]$ values decrease in absolute value when the number of C atoms increase in the molecule, and so the calculated mean value is valid for molecules with up to ten C atoms.

With the data obtained in eqs 9−11, we can now calculate the $\Delta_f H^0_m$(g) values for 3-buten-1-ol and 3-butyn-1-ol and compare the results with the values obtained experimentally in this work. The calculated values are reported in Table 11.

As it can be seen in that table, the average of the calculated $\Delta_f H^0_m$(g) values for 3-buten-1-ol and 3-butyn-1-ol is in excellent agreement with the experimental values. The estimated enthalpies of formation of 1-alkenols and 1-alkynols up to 10 C atoms are collected in Table 12. The value calculated for 2-propen-1-ol is 3.8 kJ mol^{-1} lower than the experimental one. This result and the fact that the difference between the experimental values for 2-propen-1-ol and 3-buten-1-ol is quite large, 22.8 kJ mol^{-1}, seem to suggest an error in the experimental $\Delta_f H^\circ_m$(g) of 2-propen-1-ol of 2−3 kJ mol^{-1}.

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