Facile Regeneration of Carbonyl Compounds from Semicarbazones by Potassium Bromate

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Oxidation of semicarbazones of benzaldehydes and acetophenones by potassium bromate (Br^V) yields the respective aldehyde or ketone in good yield at ambient temperature. The rates of these reactions are little influenced either by the change in substituents at the phenyl ring or by the polarity of the medium, suggesting that the intermediate for the reaction is probably as polar as the reactants. The reaction possibly proceeds *via* a preformed *N*-bromate ester in the slow step whose formation is, generally, less susceptible to electronic effects.

There are not many methods available in the literature for the regeneration of carbonyl compounds from semicarbazones under mild conditions. The reaction of thallium triacetate with semicarbazones of acetophenone and substituted acetophenones[1] yielded the carbonyl compound in *ca.* 65—90% after long reflux times with an acylated by-product. But $Tl(OAc)_3$ oxidation of benzaldehyde semicarbazones gave the respective aldehyde in 90% yield at ambient temperatures.[2] This work describes another method of regenerating carbonyl compounds quantitatively from semicarbazones, using potassium bromate (Br^V) as oxidant, at ambient temperature.

Results and Discussion

The kinetics of potassium bromate oxidation of benzaldehyde and acetophenone semicarbazones have been studied in 50% aqueous acetic acid with 0.20 mol dm^{-3} $HClO_4$ at 31 $\pm$ 0.2 °C, in the presence of 0.010 mol dm^{-3} $Hg(OAc)_2$. The Br^V reaction with semicarbazone, uncontaminated by Br_2, can be followed[3] by addition of $Hg(OAc)_2$ as it removes Br^- (one of the products of the reaction) as a complex, preventing its reaction with bromate. From the kinetic data summarised in Table 1 for these reactions, the reaction is first order in each reactant with the rate law (1).

$$-d[Br^V]/dt = k_2[Br^V] \text{[semicarbazone]} \qquad (1)$$

This is an acid-catalysed reaction and from the increase in rate with increasing $HClO_4$ concentration in the narrow range† 0.20—1.00 mol dm^{-3} at a constant ionic strength of 1.0 mol dm^{-3}, the order with respect to $HClO_4$ is deduced as 1.0 (in the range 0.20—0.70 mol dm^{-3}, Table 1) suggesting the possible reactive species as $HBrO_3$ at low concentrations. The dependence on $[H^+]$ can also be due to pre-protonation of substrate.‡

Substituent Effects.—The specific rates for Br^V oxidation of various substituted semicarbazones of benzaldehyde and aceto-phenone are not influenced much by electronic factors. Even the introduction of a strong electron-withdrawing group such as *m*-NO_2 and electron-donating group like *p*-OCH_3 has little effect on the rate of oxidation (Table 2). Also the reactivity of
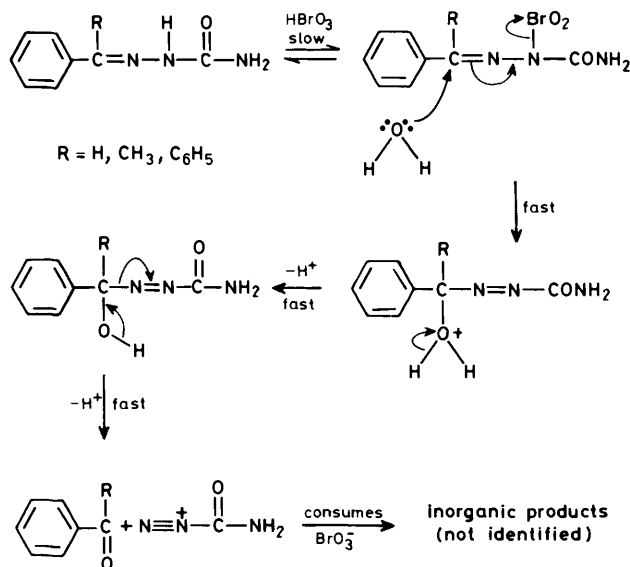
Scheme 1.

benzaldehyde semicarbazone seems to be comparable to that of benzophenone semicarbazone which has no α-C–H bond, indicating the non-participation of the α-C–H bond of benz-aldehyde semicarbazone in the slow step of the reaction. This is further corroborated by the formation of the respective alde-hyde or ketone as the product in quantitative yield at ambient temperature.

Mechanism.—To account for the product of the Br^V reaction with the semicarbazones of aldehydes and ketones and the insensitivity of the rates to substituent effects, the mechanism in Scheme 1 involving the bromate-ester formation in the rate-determining step is proposed. Scheme 1 envisages the formation of an *N*-bromate ester in a slow step, which is generally inert towards substitution[4] though the nitrogen at which bromate ester forms is in conjugation with the phenyl ring. As the specific rates of oxidation of semicarbazones of benzaldehyde, acetophenone, and benzophenone are comparable, it probably rules out the participation of an α-C–H bond in benz-aldehyde in the rate-determining step. Also as the rate of the reaction is not assisted by decreasing polarity of the medium, the transition state of this reaction is probably as polar as the reactants, which is in keeping with the mechanism proposed for this reaction.

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† The rate of decomposition–disproportionation of Br^V at $HClO_4$ acid concentrations greater than 1.0 mol dm^{-3} is considerable, making it difficult to extend this study to higher acid concentrations.
‡ The first-order dependence on $HClO_4$ concentration, in the range 0.20—0.70 mol dm^{-3}, is observed even for the Br^V oxidation of secondary alcohols. This suggests that $HBrO_3$ is a possible reactive species in this medium.

Table 1. Kinetic data for Br^V oxidation of semicarbazones [a]

R[1]	[R[2]]	$10^2[R^2C_6H_4-\overset{\overset{\displaystyle R^1}{\displaystyle \vert}}{C}=N-\overset{\overset{\displaystyle H}{\displaystyle \vert}}{N}-\overset{\overset{\displaystyle O}{\displaystyle \Vert}}{C}-NH_2]$/mol dm^{-3}	$10^3[Br^V]$/mol dm^{-3}	10^5k_1[b]/s^{-1}	10^3k_2/dm^3 mol^{-1} s^{-1}
H	H	0.50	0.50	3.0	6.0
		1.00	0.50	6.0	6.0
		2.0	0.50	12.2	6.1
		4.0	0.50	25	6.1
		1.00	1.00	6.0	6.0
		1.00	2.0	5.9	5.9
		0.50	0.50[c]	3.8	7.6
		0.50	0.50[d]	7.8	15.5
		0.50	0.50[e]	16.5	33
		0.50	0.50[f,g]	34	68
CH$_3$	H	1.00	0.50	12.3	12.3
		2.0	0.50	25	12.7
		4.0	0.50	52	13.0
		1.00	1.00	12.0	12.0
		1.00	2.0	11.8	11.8

[a] Reactions were carried out at 31 $\pm$ 0.2 °C in 50% aqueous acetic acid and 0.20 mol dm^{-3} HClO$_4$ in the presence of 0.010 mol dm^{-3} Hg(OAc)$_2$ unless otherwise mentioned. [b] $-d \ln[Br^V]/dt = k_1/s^{-1}$. [c] In 0.20 mol dm^{-3} HClO$_4$ at an ionic strength of 1.0 mol dm^{-3}. [d] In 0.40 mol dm^{-3} HClO$_4$ at an ionic strength of 1.0 mol dm^{-3}. [e] In 0.70 mol dm^{-3} HClO$_4$ at an ionic strength of 1.0 mol dm^{-3}. [f] In 1.00 mol dm^{-3} HClO$_4$ at an ionic strength of 1.0 mol dm^{-3}. [g] The specific rates of decomposition and disproportionation of bromate are 1.77 $\times$ 10^{-5} s^{-1} at 1.0 mol dm^{-3} HClO$_4$ and 7.8 $\times$ 10^{-5} s^{-1} at 2.0 mol dm^{-3} HClO$_4$ concentrations.

Table 2. Substituent effect on the rate of Br^V oxidation of semicarbazones [a]

$$R^2C_6H_4-\overset{\overset{\displaystyle R^1}{\displaystyle \vert}}{C}=N-\overset{\overset{\displaystyle H}{\displaystyle \vert}}{N}-\overset{\overset{\displaystyle O}{\displaystyle \Vert}}{C}-NH_2$$

		31 °C		55 °C
R[1]	R[2]	10^3k_2/dm^3 mol^{-1} s^{-1}	10^2k_2[b]/dm^3 mol^{-1} s^{-1}	10^2k_2/dm^3 mol^{-1} s^{-1}
H	H[c]	6.0	3.6	7.9
H	p-CH$_3$	6.8	5.4	8.1
H	p-Cl	5.5	3.1	7.4
H	m-NO$_2$	5.0	1.9	6.5
H	p-OCH$_3$	10.0	6.5	17
H	o-Cl	5.0	2.7	6.7
H	o-NO$_2$	4.8	1.8	5.1
C$_6$H$_5$	H	4.8		10.2
CH$_3$	H	9.8	5.7	15.1
CH$_3$	p-CH$_3$	10.1	5.8	15.8
CH$_3$	p-Cl	8.9	5.6	13.6
CH$_3$	p-Br	8.9	5.8	13.6
CH$_3$	p-OCH$_3$	9.5	6.0	15.5

[a] Reactions were carried out in 50% aqueous acetic acid in 0.20 mol dm^{-3} HClO$_4$ and 0.010 mol dm^{-3} Hg(OAc)$_2$ with initial concentration of reactants, [Br^V] 5.0 $\times$ 10^{-4} mol dm^{-3} and [substrate] 5.0 $\times$ 10^{-3} mol dm^{-3}. [b] The specific rates refer to the solvent composition of 70% aqueous acetic acid. [c] Under identical conditions the specific rate of Br^V oxidation of semicarbazide is 8.0 $\times$ 10^{-3} dm^3 mol^{-1} s^{-1}.

One cannot completely dismiss the alternative mechanism in Scheme 2 in which BrO$_3^-$ adds to C=N of the protonated form of semicarbazone. In a subsequent step, electron transfer to Br^V occurs along with the breaking of C–N bond yielding the carbonyl compound as one of the products. If there is an initial nucleophilic attack on carbon by BrO$_3^-$, an electron-withdrawing group such as m-NO$_2$ should facilitate the reaction and an electron-donating group such as p-CH$_3$ should retard the rate, which is not observed. Substituents such as o-NO$_2$ and o-Cl should sterically hinder such an initial attack by BrO$_3^-$. The absence of both electronic and steric effects in the rate of Br^V oxidation of semicarbazones seems to favour Scheme 1, i.e. N-bromate ester formation as a slow step.

Experimental

The aromatic aldehydes used for preparing semicarbazones were extra pure (Fluka AG–Koch Light–K and K–Aldrich)

and the corresponding semicarbazones were prepared by a literature procedure.[5] Potassium bromate, perchloric acid, acetic acid, and mercury(II) acetate were of reagent grade (B.D.H.).

The rate of this reaction was measured by estimating unchanged Br^V iodometrically[6] to a starch end-point. The specific rates evaluated using integrated rate equations from duplicate runs agreed to within $\pm$7% and these values also agreed with those obtained from graphs of logarithms of change in bromate concentration *versus* time.

Product Analysis and Stoicheiometry.—Semicarbazone was dissolved in 50% aqueous acetic acid at 31 $\pm$ 0.2 °C in 0.20 mol dm^{-3} HClO$_4$ and potassium bromate (*ca.* 9—14 mmol) in 50% aqueous acetic acid was then added. After *ca.* 9 half-lives, the mixture was diluted with equal volumes of ice and water and extracted with CHCl$_3$, in three portions. Extracts were dried (MgSO$_4$), filtered, and acetic acid was neutralised by adding

Table 3. Stoicheiometric data in the Br^V oxidation of semicarbazones [a]

$10^3[C_6H_5\text{-}\overset{R}{\underset{}{C}}\text{=}N\text{-}\overset{H}{\underset{}{N}}\text{-}\overset{O}{\underset{}{C}}\text{-}NH_2]/$ mol dm^{-3}	$10^2[Br^V]_{initial}/$ mol dm^{-3}	$10^2[Br^V]_{final}/$ mol dm^{-3}	$10^3\Delta[Br^V]$[b]/ mol dm^{-3}	$10^3[\overset{O}{\underset{}{-C-}}]/$ mol dm^{-3} (%)
R = H				
5.0	2.0	1.37	5.0	3.4 (68)
7.5	2.0	1.09	7.8	5.3 (70)
10.0	2.0	0.94	9.3	6.8 (68)
R = CH$_3$				
5.0	2.0	1.37	5.0	4.1 (82)
10.0	2.0	1.12	8.0	8.0 (80)
R = C$_6$H$_5$				
5.0	2.0	1.58	4.0	4.2 (84)
10.0	2.0	1.11	8.0	8.5 (85)

[a] These reactions were carried out in 50% aqueous acetic acid in 0.20 mol dm^{-3} HClO$_4$ and 0.020 mol dm^{-3} Hg(OAc)$_2$ at 31 $\pm$ 0.2 °C. [b] The change in concentration of Br^V due to its reaction with semicarbazone has been calculated after applying due blank corrections for the self-decomposition–disproportionation of Br^V at this concentration, which comes to nearly 6.5% of $[Br^V]_{initial}$.

Scheme 2.
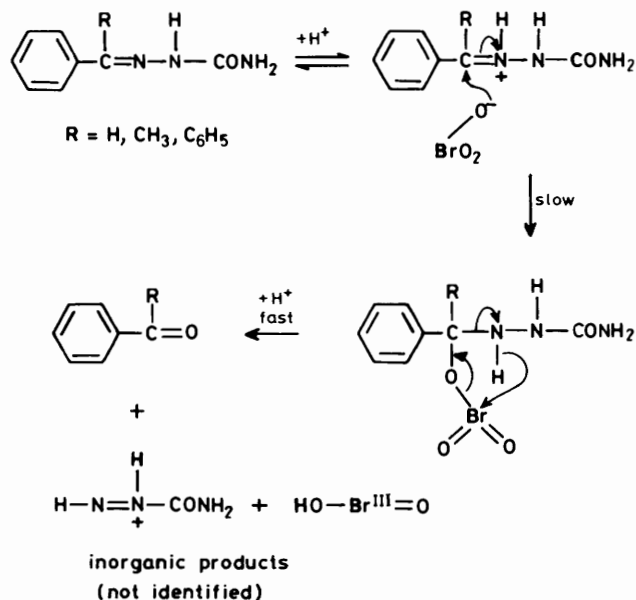
saturated NaHCO$_3$ solution. The organic product was then extracted with ether. From the u.v. and i.r. spectra, it has been identified as the corresponding aldehyde or ketone. The amount of benzaldehyde, benzophenone, or acetophenone formed was determined by measuring the absorbance for the ether extracts at 250 (ε 11 400 dm^3 mol^{-1} cm^{-1}), 257 (18 500), or 246 nm (12 600),[7,8] respectively. The inorganic products were not identified.

The stoicheiometric results are summarised in Table 3. The yield of benzaldehyde is only 70% as it is partly further oxidised to benzoic acid. As bromate does not oxidise ketones under the reaction conditions, the yield of acetophenone is 80% and that of benzophenone 85%.

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