Kinetics and mechanism of the oxidative regeneration of carbonyl compounds from phenylhydrazones by [bis(trifluoroacetoxy)iodo]benzene

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The oxidation of several aldo- and keto-phenylhydrazones by [bis(trifluoroacetoxy)iodo]benzene (TFAIB), in aqueous acetic acid leads to the regeneration of the parent carbonyl compounds. The reaction exhibits a first order dependence on both the phenylhydrazone and TFIAB. The oxidation of ketoximes is slower than that of aldoximes. The oxidation of aliphatic phenylhydrazones correlates well in terms of Pavelich–Taft dual substituent-parameter equation. The low positive value of the polar reaction constant indicates a nucleophilic attack by TFIAB on the carbonyl carbon. The reaction is subject to steric hindrance by the alkyl group. A mechanism involving the formation of a cyclic activated complex in the rate-determining step is proposed.

Keywords: carbonyl compounds, phenylhydrazones, [bis(trifloroacetoxy)iodo] benzene

Regeneration of carbonyl compounds from their derivatives under mild conditions is an important process in synthetic organic chemistry. Several oxidative methods are available for regeneration from phenylhydrazones and hydrazones.[1] Hypervalent iodine compounds are mild and selective oxidizing agents and their use in organic synthesis has been described recently.[2] There seems to have been no report about the kinetics of oxidative regeneration from hydrazones by hypervalent iodine compounds, though the synthetic aspects of the regeneration of carbonyl compounds from hydrazones and similar derivatives by TFIAB and [bis(acetoxy)iodo] benzene have been studied.[3] We report here the kinetics of oxidative regeneration of several aldehydes and ketones from their phenylhydrazones by TFIAB in aqueous acetic acid solution.

Experimental

Phenylhydrazones were prepared by the reported standard methods and their m.p. were checked with the literature values. TFAIB was a commercial product (Aldrich) and was used as supplied. Acetic acid was purified by refluxing it with chromium trioxide and acetic anhydride for 3 h and then distilling it.

Product analysis: The oxidation of phenylhydrazones results in the regeneration of corresponding carbonyl compounds, as confirmed by TLC (eluent: CCl_4/Et_2O). Isolation of the product was attempted in the oxidation of phenylhydrazones of benzaldehyde and acetophenone. In a typical experiment, the phenylhydrazone (0.2 mol) and TFAIB (0.02 mol) were dissolved in 50 ml of 1:1 (v/v) acetic acid–water, and allowed to stand for *ca.* 10 h for the completion of the reaction. Silica gel (5 g) was then added and the reaction mixture was stirred for 15 min.[4] It was then filtered and the solid residue was washed with the solvent (2 × 15 ml). The solvent was removed on a rotary evaporator and the residue was purified on a silica-gel column (eluent: CCl_4/Et_2O). Evaporation of the solvent afforded the pure carbonyl compound. Yields of benzaldehyde and acetophenone were 1.83 g (86%) and 2.14 g (89%) respectively.

Kinetic measurements: The reactions were studied under pseudo-first order conditions by keeping a large excess (× 10 or greater) of the phenylhydrazone over TFAIB. The solvent was 1:1 (v/v) acetic acid–water, unless mentioned otherwise. The reactions were studied at constant temperature (±0.1 K). The reactions were followed by monitoring the decrease in the concentration of TFAIB by an iodometric method. The pseudo-first order rate constant, k_{obs}, was evaluated from the linear ($r^2 > 0.995$) least-squares plots of log [TFAIB] versus time. Duplicate runs showed that the rate constants were reproducible to within ±4%. The second order rate constant, k_2, was calculated from the relation: $k_2 = k_{obs} / $ [phenylhydrazone]. We have used coefficient of determination (R^2 or r^2), standard deviation (SD) and Exner's[5] parameter, ψ, as the measures of goodness-of-fit in correlation analysis.

Results

The analysis of products indicated the following overall reaction.

$$R_2 C = N - NHPh + PhI(OCOCF_3)_2 + H_2O \rightarrow$$
$$R_2 C = O + HN = N - Ph + PhI + 2CF_3COOH \quad (1)$$

Induced polymerisation of acrylonitrile: The oxidation of acetaldo-phenylhydrazone by TFAIB, in an atmosphere of nitrogen, failed to induce polymerisation of acrylonitrile. In blank experiments, with the hydrazone absent, no noticeable consumption of TFAIB was observed. To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm^{-3} of 2,6-di-t-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively. Further, the addition of acrylonitrile had no effect on the rate of oxidation (Table 1). This indicates that a one-electron oxidation, giving rise to free radicals, is unlikely in this reaction.

The reaction is first order respect to TFAIB. The individual kinetic runs yielded linear ($r^2 > 0.995$) plots between log [TFAIB] and time. Further, the values of k_{obs} do not depend on the initial concentration of TFAIB. The reaction exhibited a linear dependence on the concentration of the phenylhydrazones (Table 1).

The oxidation of the phenylhydrazones was studied in solutions containing different proportions of acetic acid and water. It was observed that the rate of oxidation decreases with an increase in the amount of acetic acid in the solvent mixture (Table 2).

Table 1 Rate constants for the oxidation of acetaldophenyl-hydrazone by TFAIB at 298 K

10^3[TFAIB]/ mol dm^{-3}	[phenylhydrazone]/ mol dm^{-3}	$10^4 k_{obs}$ /s^{-1}
1.0	0.1	7.14
1.0	0.2	14.3
1.0	0.4	28.6
1.0	0.6	42.7
1.0	1.0	71.7
1.0	1.4	101
1.0	1.7	122
0.5	0.6	42.6
2.0	0.6	43.1
3.0	0.6	42.0
5.0	0.6	43.3
6.0	0.6	42.5
1.0	0.6	42.5[a]

[a]Contained 0.003 mol dm^{-3} acrylonitrile

Table 2 Dependence of the reaction rate on solvent composition

% HOAc (v/v)	25	50	60	75
$10^4 k_{obs}$ / s^{-1}	37.8	28.6	23.9	15.8

[TFAIB] = 0.001 mol dm^{-1}, [acetaldophenylhydrazone] = 0.4 mol dm^{-1}, Temp. = 298 K

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* Correspondence.

Table 3 Rate constants and activation parameters of the oxidation of phenylhydrazones (R^1R^2 C = N-NHPh) by TFAIB

Substituents		$10^4 \, k_2$/ dm³ mol⁻¹ s⁻¹				ΔH^*	ΔS^*	ΔG^*
R^1	R^2	288 K	298 K	308 K	318 K	kJ mol⁻¹	J mol⁻¹ K⁻¹	kJ mol⁻¹
H	H	1460	1970	2860	4000	23.3±0.8	−181±3	76.9±0.6
H	Me	52.4	71.7	116	185	29.6±1.8	−186±5	85.0±1.4
H	Et	31.3	51.1	85.1	131	34.2±0.3	−174±1	86.1±0.3
H	Pr	16.7	27.3	45.3	73.2	35.1±0.5	−177±2	87.5±0.4
H	i-Pr	10.2	17.0	29.8	53.4	39.5±1.2	−166±4	88.7±0.9
H	ClCH₂	98.5	142	203	303	25.8±0.7	−194±2	83.5±0.5
H	Ph	212	292	423	580	23.3± 0.5	−197±2	81.7±0.4
Me	Me	1.25	2.23	4.01	7.27	42.1±0.8	−174±3	93.8±0.6
Me	Et	0.96	1.85	3.30	6.03	43.9±0.4	−170±2	94.3±0.3
Et	Et	0.78	1.31	2.45	4.61	42.7±1.6	−176±5	95.0±1.3
Me	Ph	7.35	12.5	21.5	35.3	37.4±0.4	−175±1	89.5±0.3

The rate constants were determined at different temperatures and the activation parameters were calculated (Table 3).

Discussion

There is no significant compensation effect[6] between the enthalpies and entropies of activation of the oxidation of the eleven phenylhydrazones ($r^2 = 0.5836$, SD = 4.92 and $\psi = 0.68$). However, a linear isokinetic relationship was obtained by using Exner's[7] method. An Exner[7] plot between log k_2 at 288 K and at 318 K, for the 11 compounds, is linear ($r^2 = 0.9987$, sd = 0.03, $\psi = 0.04$; slope = 0.873 ±0.012). The value of the isokinetic temperature is 1487±65 K. A linear isokinetic relationship is a necessary condition for the validity of linear free energy relationships. It also implies that all reactions so correlated follow a similar mechanism.[7]

We could not find any report about the kinetics of the reaction between a hydrazone and a diacyloxyiodobenzene, although Barton *et al.*[3] have studied the synthetic aspects of the reaction between phenylhydrazones of keto-esters and TFAIB. They have suggested a probable mechanism. Alkenes are not usually subject to nucleophilic attack. However, carbon–nitrogen bonds, being dipolar in nature can be easily attacked by a nucleophile. The data in Table 3 showed that the rate of oxidation of ketophenylhydrazones is much less compared to that of aldophenylhydrazones. The reason for the slower reaction of the ketophenylhydrazones may be steric. As the central carbon changes from a trigonal to a tetragonal state, the crowding around it increases. This increase will be more in the case of ketophenylhydrazones as compared to aldophenylhydrazones. This observation is supported by the correlation analysis of the reactivity of aliphatic hydrazones. The rate of oxidation of aliphatic hydrazones did not yield significant correlation separately with Taft's σ^* and E_s values (eqns 2 and 3). The rates were, therefore, correlated with Pavelich–Taft's[8] dual substituent-parameter eqn (4).

$$\log k_2 = 0.82 \pm 0.35 \, \Sigma\sigma^* - 3.06 \tag{2}$$
$r^2 = 0.4367$, SD = 0.83, $n = 9$, $\psi = 0.80$, Temp. = 298 K

$$\log k_2 = 1.22 \pm 0.10 \, \Sigma E_s - 3.96 \tag{3}$$
$r^2 = 0.9592$, SD = 0.22, $n = 9$, $\psi = 0.21$, Temp. = 298 K

$$\log k_2 = \rho^* \Sigma \, \sigma^* + \delta \Sigma \, E_s + \log k_o \tag{4}$$

The rates exhibited excellent correlations in terms of Pavelich–Taft equation (Table 4). The reaction constants have positive values.

It is of interest to compare the results of the correlation in this reaction with previously reported data on the reactions of carbon-hetero atom double bonds. Nucleophilic additions to C = O and C = N bonds usually results in large positive polar reaction constants *e.g.* base-catalysed hydrolysis of N-

Table 4 Dependence of reaction constants of the oxidation of aliphatic phenylhydrazones by TFAIB on temperature

Temp/K	ρ^*	δ	R^2	SD	ψ
288	0.30±0.02	1.12±0.02	0.9989	0.04	0.04
298	0.29±0.01	1.08±0.01	0.9994	0.03	0.03
308	0.26±0.01	1.05±0.01	0.9997	0.02	0.02
318	0.24±0.01	1.01±0.01	0.9996	0.02	0.02

No. of compounds = 9

substituted benzylideneanilines[9] exhibits a $\rho \approx 2.7$ and in the addition of HCN to aromatic aldehydes,[10] ρ has a value of 2.3. Similarly, the base-catalysed hydrolysis of phenyl benzoates[11] exhibited a reaction constant of 1.76 at 298 K. The value of composite ρ in the base-catalysed hydrolysis of disubstituted benzils[12] is 5.7 (migrating $\rho = 3.85$ and non-migratory $\rho = 1.85$). Not many such reactions aliphatic compounds have been studied. The base-catalysed hydrolysis of methyl esters has been correlated[13] in terms of Pavelich–Taft's equation. The values of polar and steric reaction constants are 1.54 and 0.71 respectively *i.e.* the reaction is more susceptible to polar effects but less to steric effects as compared to the reaction investigation. However, in the reactions involving a cyclic activated complex, the polar reaction constants have low magnitudes. In chromic acid oxidation of aromatic aldehydes,[14] where the decomposition of a chromate ester *via* a cyclic transition state has been proposed, the value of ρ is *ca* 1. Similarly, the addition of methyl magnesium bromide to 1-aryl-2-phenylpropanones[15] exhibited a $\rho = 0.24$. This reaction may proceed through a four-centre cyclic transition state. In the oxidative regeneration of aliphatic aldehydes from the corresponding oximes, by cetyltrimethylammonium permanganate,[16] the values of the polar and steric reaction constants are 0.46 and 1.10 respectively at 298 K. Similarly, the oxidation of aldoximes by tetrabutylammonium tribromide exhibited $\rho^* = 0.64$ and $\delta = 0.84$ at 298 K.[17] These reactions may involve a nucleophilic attack by the permanganate-oxygen and tribromide ion respectively on the C = N bond through a cyclic transition state.
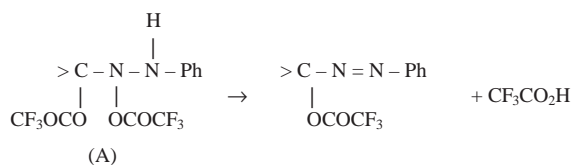
Therefore, the observed low positive reaction constant, in the present reaction, points to a cyclic transition state in which the formation of bond between the trifluoroacetoxy-oxygen and the carbon is somewhat ahead of the formation of N – O bond. This supports a nucleophilic attack by a trifluoroacetoxy-oxygen on the carbon. The positive steric reaction constant points to a steric hindrance by the substituents. The fact that the steric effects are greater in this reaction than in the attack of a hydroxide on methyl esters[13] further supports the formation of a cyclic activated complex in the oxidation of phenylhydrazones by TFAIB. Therefore, the following mechanism (Scheme 1) is proposed for the reaction. The mechanism is supported by the values of the activation parameters also. The low values of

enthalpy of activation indicate that the bond-cleavage and bond formation are almost synchronous. The large negative entropies of activation support the formation of a rigid cyclic activated complex from two acyclic molecules. Table 3 shows that the enthalpies of activation of the oxidation of phenylhydrazones exhibited a narrow range (33±10 kJ mol^{-1}). The entropies of activation vary from –166 to –197 J K^{-1} mol^{-1}.

The oxidation of aldophenylhydrazones showed a large variation in the rate (*ca* 140 times). Though both polar and steric effects of the substituent are responsible for the observed variation in the rate, the contribution of the steric factor is greater (*cf*. Table 4). However, amongst the ketophenyl-hydrazones the variation in rate is not that sharp. The slowest and fastest differ by a factor of *ca* 10 only. In fact, the variation in the structure of among the ketophenylhydrazones is not very appreciable. The difference in the polar and steric effects of methyl and ethyl groups is not much. Phenyl group is relatively bulky but its resonance effect may cancel out its steric effect on the rate.

The small increase in the reaction rate with an increase in the polarity of the medium also supports the proposed mechanism. The transition state involves a weakly electron-deficient carbon centre. Thus the transition state is slightly more polar than the reactants.

Barton *et al.*[3] have proposed a different mechanism on the basis of synthetic studies on the oxidation of phenylhydrazones of α-keto-esters by TFAIB. They observed that in aqueous acetonitrile, the oxidation of the phenylhydrazones by TFAIB yielded an α-acyloxyphenylazo compound and the parent carbonyl compound. They have suggested the formation of a common intermediate, which underwent decomposition by different pathways forming the two products. We suggest that the intermediate (A) may also yield the α-acyloxyphenylazo compound by the following pathway.

$$> C - \underset{\underset{CF_3OCO \quad OCOCF_3}{|\quad\quad\;|}}{\overset{\overset{H}{|}}{N}} - N - Ph \quad \rightarrow \quad > C - \underset{\underset{OCOCF_3}{|}}{N} = N - Ph \quad + CF_3CO_2H$$

(A)

Received 19 February 2004; accepted 6 March 2004
Paper 04/2352

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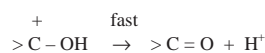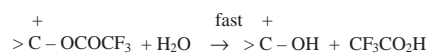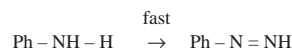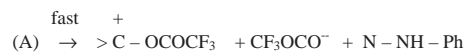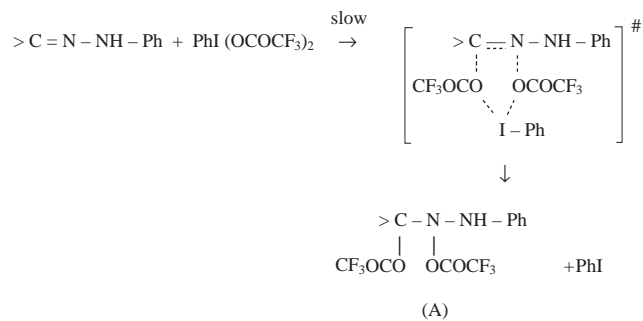
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$$> C = N - NH - Ph \; + \; PhI(OCOCF_3)_2 \quad \overset{slow}{\rightarrow} \quad \left[\begin{array}{c} > C \cdots N - NH - Ph \\ \vdots \quad\quad \vdots \\ CF_3OCO \quad OCOCF_3 \\ \\ I - Ph \end{array} \right]^{\#}$$

$$\downarrow$$

$$> C - \underset{\underset{CF_3OCO \quad OCOCF_3}{|\quad\quad\quad|}}{N} - NH - Ph \quad\quad\quad + PhI$$

(A)

$$(A) \quad \overset{fast}{\rightarrow} \quad > \overset{+}{C} - OCOCF_3 \; + CF_3OCO^- \; + \; N - NH - Ph$$

$$Ph - NH - H \quad \overset{fast}{\rightarrow} \quad Ph - N = NH$$

$$> \overset{+}{C} - OCOCF_3 \; + H_2O \quad \overset{fast}{\rightarrow} \quad > \overset{+}{C} - OH \; + \; CF_3CO_2H$$

$$> \overset{+}{C} - OH \quad \overset{fast}{\rightarrow} \quad > C = O \; + \; H^+$$

Scheme 1