Thermodynamics of adsorption and desorption of hydrogen sulfide in micropores of activated carbon

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Summary. Thermodynamics of adsorption and desorption of hydrogen sulfide in micropores of activated carbon have been studied on the basis of q and ΔS. The values of q and ΔS of adsorption were larger than those of desorption.

It has been shown the equation describing adsorption on non-porous adsorbent is the Gibbs equation, while the equation describing adsorption in micropores is the Gibbs-Duhem equation[2]. Dubinin and Astakhov[3] reported a thermodynamic equation for adsorption well fitted to express the characteristics of gas adsorption by a porous adsorbent on the basis of the potential theory of Polanyi[4]. According to Bering et al.[5] and Dubinin[2], it is possible to write the following expressions for the net differential heat of adsorption $q = E\,[(\ln a_0/a)^{1/n} + \alpha T/n\,(\ln a_0/a)^{1/n-1}]$ and for the differential molar entropy of adsorption $\Delta S = -\alpha E/n\,(\ln a_0/a)^{1/n-1}$, where E is the characteristic energy of adsorption at the characteristic point, a_0 is the limiting amount adsorbed, a is the amount adsorbed at different equilibrium pressure, n is a constant, and α is the coefficient of thermal expansion of hydrogen sulfide. In a previous paper it was shown that the adsorption of hydrogen sulfide on activated carbon resulted in volume filling of the micropores[6]. The present paper describes the thermodynamic properties of adsorption and desorption of hydrogen sulfide in micropores of activated carbon on the basis of the dependence of q and ΔS on the degree of filling of micropores.

Materials and methods. The purity of hydrogen sulfide gas was indicated to be 99.9%. Activated carbon was a commercial product and its physical properties are as follows: particle size, 32–48 mesh; specific surface area, 892.8 m^2/g; pore volume, 0.5039 ml/g; mean pore radius, 11.29 Å; true specific gravity, 2.17 g/ml; element analysis, H: 0.38%, C: 87.82%, N: 4.31%; pH of suspension of activated carbon, 6.7. The procedures for adsorption and desorption were described previously[6]. The values of q and ΔS were calculated from the experimental results of adsorption and desorption isotherms (fig. 1).

Results and discussion. The adsorption and desorption isotherms of hydrogen sulfide on activated carbon (fig. 1) showed that the hysteresis phenomena were temperature-dependent, and that the hysteresis loops increased in size with increasing temperature. The values of q of adsorption and desorption (fig. 2) decreased with increasing degree of filling of micropores. According to the potential theory developed by Dubinin et al.[7], the results (fig. 2) suggest that the micropores of activated carbon are consecutively filled with hydrogen sulfide from smallest pores to large pores, and that hydrogen sulfide adsorbed is desorbed from large pores to smallest pores. The results (fig. 3) indicate that the entropy of adsorption and desorption becomes small with an increase in the degree of filling. This entropy change suggests that the hydrogen sulfide molecule is compactly filled in the micropores with increasing degree of filling, that is, the molecule is possibly immobilized in the micro-

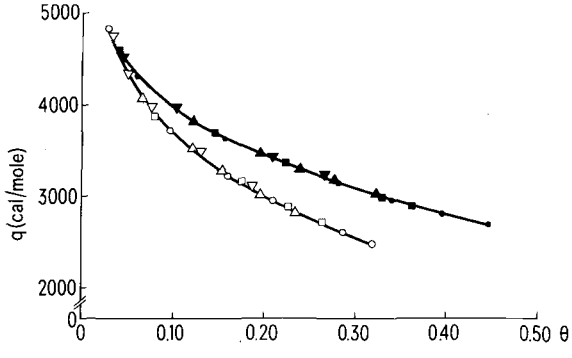

Figure 2. Dependence of net differential heat of adsorption and desorption of hydrogen sulfide on the degree of filling of micropores. Closed symbols and open symbols denote the net differential heat of adsorption and desorption, respectively. q is the net differential heat of adsorption and desorption of hydrogen sulfide and θ is the degree of filling of micropores ($\theta = W/W_0$, W is the filled volume of the adsorption space, W_0 is the limiting volume of the adsorption space). ●, ○ :20 °C; ■, □ :30 °C; ▲, △ :40 °C; ▼, ▽ :50 °C.

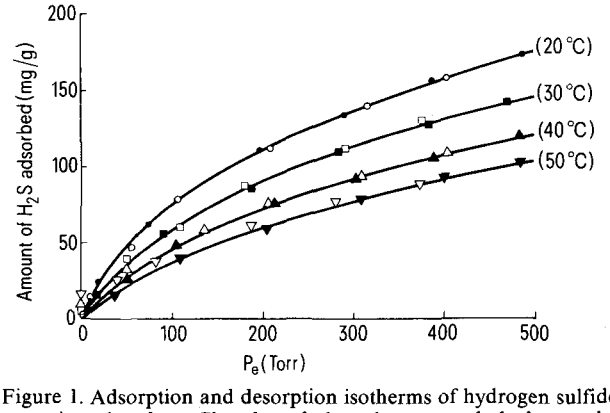

Figure 1. Adsorption and desorption isotherms of hydrogen sulfide on activated carbon. Closed symbols and open symbols denote the experimental data of adsorption and desorption isotherms, respectively. The equilibrium amounts adsorbed at different equilibrium pressures were determined within an error of 0.5%. P_e is the equilibrium pressure of hydrogen sulfide.

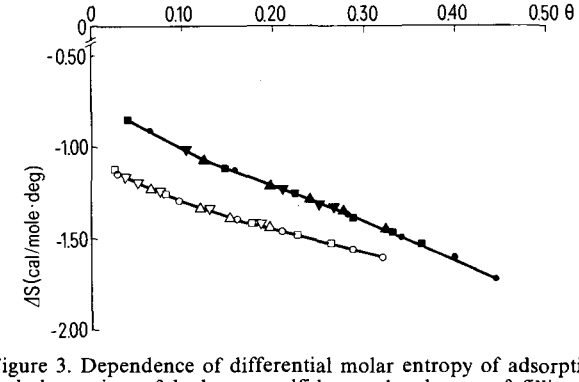

Figure 3. Dependence of differential molar entropy of adsorption and desorption of hydrogen sulfide on the degree of filling of micropores. Closed symbols and open symbols denote the differential molar entropy of adsorption and desorption, respectively. ΔS is the differential molar entropy of adsorption and desorption and θ is the degree of filling of micropores. ●, ○ :20 °C; ■, □ :30 °C; ▲, △ :40 °C; ▼, ▽ :50 °C.

pores with increasing adsorption. The fact that the entropy of desorption is smaller than that of adsorption (fig. 3) can be explained by the ink bottle theory of adsorption hysteresis suggested by Kraemer and McBain[8], and suggests that the activated carbon used has micropores with narrow entrance and wide interior.

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o-Aminoacetophenone: Identification in a primitive fungus-growing ant *(Mycocepurus goeldii)*

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Summary. *o*-Aminoacetophenone is the major volatile product present in the mandibular gland secretion of the primitive fungus-growing ant *Mycocepurus goeldii*. This novel arthropod natural product is biosynthetically far removed from the aliphatic ketones and alcohols found in those genera of the tribe Attini that represent the main line of evolution. The divergent phylogenetic position of *Mycocepurus*, and possibly of other closely related genera, is emphasized.

Recent investigations[2-6] on the natural products chemistry of attine ants have demonstrated that these hymenopterans are a rich source of 2- and 3-alkanones, the corresponding alcohols, and in some cases, oxygenated monoterpenes. The ethyl ketones, which are the main releasers of alarm behavior in species in the more highly evolved genera[2,5], are generally the major compounds produced in the mandibular glands. An investigation[5] of the mandibular gland products of fungus-growing ants in several genera that reflect the accepted phylogeny of the tribe Attini[7] indicates that the distribution of these exocrine compounds is in accord with the recognized evolution of the genera in this taxon. However, whereas this chemosystematic study utilized species in genera whose established relationships clearly defined them as pivotal taxa in the phylogeny of the tribe[8], it did not include species in the small genera that appear to have diverged from the general attine stem[7]. We now wish to report that the mandibular gland chemistry of *Mycocepurus goeldii*[9], a species in one of these divergent genera, is dominated by *o*-aminoacetophenone, an exocrine compound unique to the tribe Attini or for that matter, to any other arthropod species.

Materials and methods. Colonies of *M. goeldii* were collected near Presidente Prudente, Brazil. Crushed heads of workers possess a strong grape-like fragrance and in southern Brazil these ants are sometimes referred to as the 'formica perfume' (perfume ant). Extracts were prepared either by dissecting mandibular glands or by crushing heads in spectrograde *n*-pentane; volatile compounds were resolved gas-chromatographically on both 1% OV-1, programmed from 100–250 °C at 5 °C/min, and 10% Carbowax 20 M, isothermally at 180 °C. Eluting compounds were collected on graphite and their mass spectra obtained by direct insertion into the ion source of a Bell and Howell 21-490 mass spectrometer.

Behavioral studies were undertaken on either field or laboratory colonies by exposing the ants to mandibular gland extracts, crushed heads, or pure compounds applied to filter paper squares (1 cm^2) or to the tips of wood applicator sticks. The activity of compounds as alarm releasers for another attine species, *Atta texana*, was determined as described previously[2,10].

Results. Four compounds, all present in mandibular gland extracts, were detected by gas chromatography, the major and final eluting one possessing the grape-like odor associated with *M. goeldii*. The mass spectrum of this compound was characterized by a molecular ion and base peak at *m/z* 135, with major fragments being present at m/z 120 (loss of CH_3), *m/z* 92 (further loss of $-COCH_3$), and *m/z* 65 (aromatic ring). The mass spectrum and retention times of this substance were completely congruent with those of authentic *o*-aminoacetophenone.

Three minor constituents, eluting earlier than aminoacetophenone, were not conclusively identified. The mass spectrum of the 1st of these compounds, possessing a strong molecular ion at *m/z* 150 and a base peak at *m/z* 135, was similar to o-methoxyacetophenone, but differed in minor respects. The other 2 compounds possessed molecular ions at *m/z* 218 and m/z 232, and their mass spectra were very similar to homofarnesene and bishomofarnesene[11]. Insufficient quantities of these compounds prevented their complete characterization.

Workers of *M. goeldii* are attracted to a crushed mandibular gland or head and respond similarly to 1 µg of *o*-aminoacetophenone placed on filter paper squares or tips of wood applicators. One the other hand, workers of the highly evolved attine species *Acromyrmex nigra, Atta laevigata* and *A. sexdens* do not appear to react to a crushed head of *M. goeldii*. High concentrations of *o*-aminoacetophenone are repellent to workers of *M. goeldii* whereas workers of the *Acromyrmex* and *Atta* species are slightly attracted to high concentrations of this compound. *o*-Aminoacetophenone was completely inactive as a releaser of alarm behavior for workers of *Atta texana* when compared at all concentrations to their natural alarm pheromone, 4-methyl-3-heptanone[1,10].

Discussion. The production of *o*-aminoacetophenone by workers of *M. goeldii* demonstrates that the exocrine chemistry of this fungus-growing ant differs considerably from those in genera representing the main line of attine evolution. Whereas aliphatic compounds such as 3-octanol and 4-methyl-3-heptanone are typical of the mandibular gland products identified in a variety of attine genera[4,5], aromatic natural products are clearly atypical of species in